

# A Study on the Variability of Fresh Diesel from Service Station in Kota Bharu Using GC-MS and PCA

Muhammad Suffian Azah, Ahmad Fahmi Lim Abdullah<sup>a</sup>

<sup>a</sup> Forensic Science Programme, School of Health Sciences, Health Campus, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia

**ABSTRACT:** The variability of the diesel population in Kota Bharu was investigated in this paper. Discrimination of diesel samples was performed by gas chromatography-mass spectrometry (GC-MS). Subsequent statistical analyses of these data were performed including principal component analysis. A data set containing 41 peaks from extracted ion chromatograms normalized to n-22 was used and diesel sample distribution pattern was visualized in the score plot. The results show that GC-MS analyses were able to discriminate different fresh diesel samples into a few groups. Among the diesel samples collected from service station on the same day, Petronas diesels were significant different from Caltex, Mobil, Esso and most of Shell samples. Diesel samples collected from a selected service station over a time scale of weeks varied significantly by GC-MS. Care must be exercised when interpreting data showing similarities or differences in GC-MS profile as to the source where the sample could have come from.

**Keywords:** Diesel, GC-MS, principal component analysis

## Introduction

Diesel is one of the refined products of crude oil that has been used worldwide as one of the fuels for motor vehicle. Most heavy load vehicles use diesel as the fuel compared to other type of fuel. In Malaysia, diesel fuels are subsidised by the government for selected sectors such as land and sea transportation as well as for fishing boats. The price is therefore significantly cheaper compared to the neighbouring countries. Crimes relating to diesel smuggling and abused of fuel-subsidy system are often reported and therefore it may be necessary to compare a seized diesel sample believed to be subsidized by the government to its known source when an offence is suspected. Also, diesel may be discharged into the environment and the ability to identify the party responsible for the spill is important. One technique used to establish the link between a question diesel to its source is via diesel fingerprinting (Stout *et al.*, 2002, Daling *et al.*, 2003)

Gas chromatography mass-spectrometry (GC-MS) is commonly used in hydrocarbon analysis as it also allows more detail characterization and identification of the sample besides giving the description of the distribution of dominating hydrocarbon in the sample (Wang, 1997, Wang *et al.*, 2003, Wang *et al.*, 2007, ASTM D 5739-06). Following GC-MS analysis, two chromatograms can be visually compared using specific extracted ions chromatograms but there might be a risk of subjective error associated with visual comparison of spectra (Hibbert *et al.*, 2008). The use of statistical analysis is therefore useful in discriminating petroleum origin (Stout *et al.*, 1991, Abdullah, 2004, Hupp *et al.*, 2008). One of the statistical analysis that can be used in exploratory nature is principal component analysis (PCA). It is a multivariate statistical analysis widely used in science and engineering fields that transforms the original data set into new, smaller, and uncorrelated variables called principal component.

This study investigates the variability of diesel fuels collected from service stations in the district of Kota Bharu, Kelantan. Principal Component Analysis (PCA) was used to discriminate the 41 selected peaks of each of the chromatograms from the 27 samples studied. One service station was arbitrarily chosen where diesel samples were collected in one-week interval over a period of four weeks to observe the variability of the diesel fuels.

Corresponding Author:

Ahmad Fahmi Lim Abdullah  
Forensic Science Programme  
School of Health Sciences  
Health Campus, Universiti Sains Malaysia  
16150 Kubang Kerian, Kelantan  
Email: [fahmilim@kb.usm.my](mailto:fahmilim@kb.usm.my)

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## Materials and Method

### Sampling

Sampling was carried out in such a way that all the samples were collected in a day. A Shell service station was sampled four times in an interval of a week for each sampling to investigate the diesel profiles over time. Prior to sampling, about 100 mL of diesel was dispensed into a metal can to flush out any contaminant at the pump. Then, a brown bottle was used to contain about 200 mL of diesel. The bottle was then capped and labeled.

1  $\mu\text{L}$  of diesel was transferred using a 10  $\mu\text{L}$  syringe into a GC vial and diluted with 1 mL of n-hexane (HPLC grade) prior to analysis. The samples were capped and labeled prior to GC analysis.

The analyses of samples were performed using a Varian CP-3800 gas chromatograph with a Varian Saturn 2200 mass spectrometer. The GC-MS is equipped with a VF-5MS fused-silica capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ , Varian). Helium was used as the carrier gas with a flow rate of 0.8 mL  $\text{min}^{-1}$ . The injection volume for each sample was 1  $\mu\text{L}$  delivered by syringe with a splitless mode for 45 sec before being vented. The temperature in the inlet and transfer line was held at 280°C. The temperature of the oven was initially held at 65°C for 5 min followed by a ramp to 300°C at 5°C  $\text{min}^{-1}$  with a final hold time of 10 min,

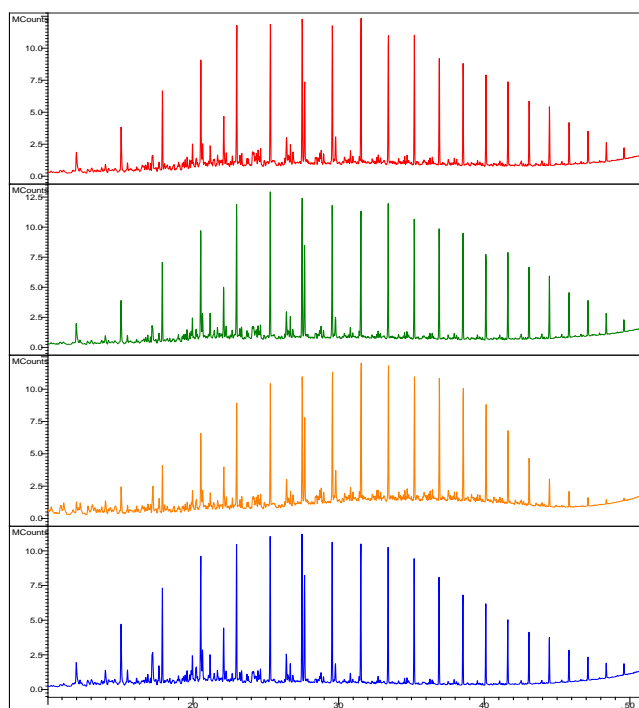
giving a total run time of 62 min. Electron-impact ionization (70 eV) was utilised with a quadrupole mass analyzer operated in full-scan mode (40 to 450  $m/z$ ).

### Data analysis

The peak selection was based on the previous study (Abdullah, 2004) and Nordtest method (Nordtest, 1991). A total of 41 peaks were selected from 13 extracted ion chromatograms that resolved clearly. All the area of selected peaks were normalised to 2,3,5-trimethylphenanthrene with a retention time at 35.88 minutes (labeled as 220b, **FIG. 3**). The data was log-transformed prior to Principal Component Analysis using XLSTAT –Pro(Win) incorporated into Windows Excel®.

## Results and Discussion

**FIG. 1** shows an overlay of chromatograms of four fresh diesel samples from Esso (E1), Caltex (C3), Shell (S1) and Petronas (P20). The chromatograms are dominated by resolved hydrocarbons consisting of n-alkanes and iso-prenoids. The n-alkanes range from n-C10 to n-C31 with a maximum at n-C16 to n-C18. The chromatograms also contain a large amount of “grass” which is unresolved complex mixture of hydrocarbons. Visual examination on total ion chromatogram may be difficult without a more careful and systematic comparison between the samples.

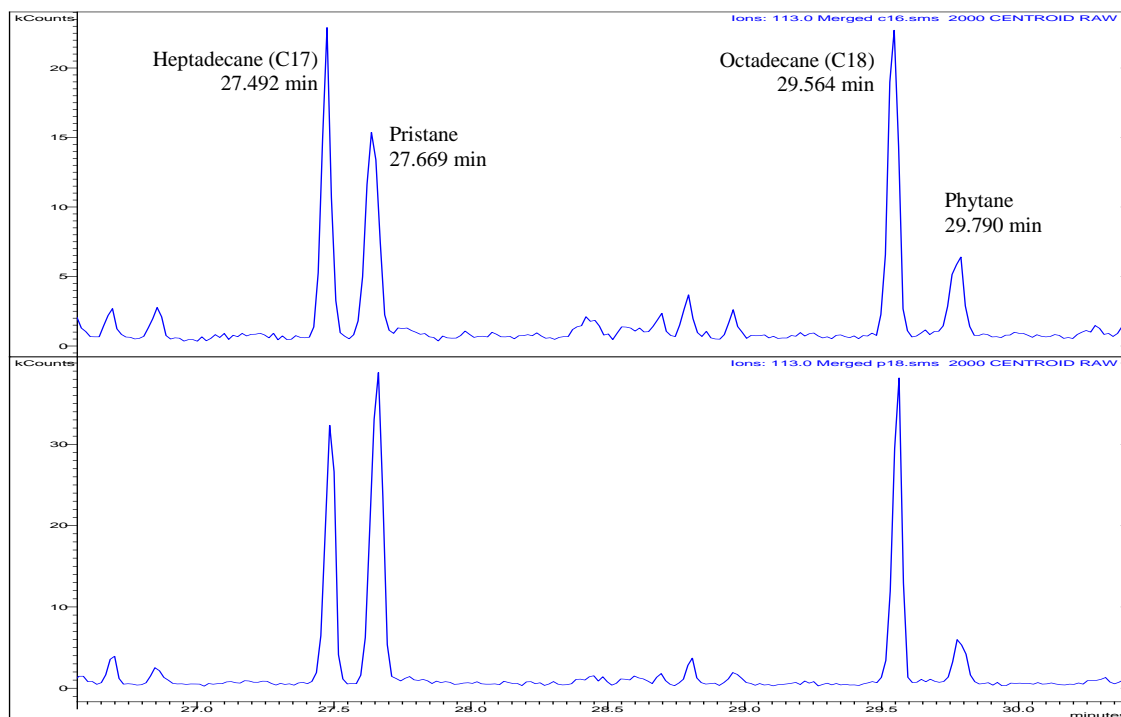


**FIG. 1-** Total ion chromatograms of Esso, Caltex, Shell and Petronas Diesel, from top to bottom.

The GC-MS software allows selected ions to be extracted using MS Workstation<sup>®</sup>. An extracted ion chromatogram looks “cleaner” than the total ion chromatogram and makes peak integration easier. **FIG. 2** shows a stack of two selected ion chromatograms showing heptadecane, pristane, octadecane and phytane from different samples. The distribution of pristane and phytane at different intensity indicated that the diesel samples were from different origin. Note that the ratios of these compounds had been used as an indicator to

exclude a sample as a potential source or provide supporting evidence of a source (Stout *et al.*, 2002). Wang *et al.* found that the ratios of n-C17/pristane, and n-C18/phytane, and pristane/phytane were unaltered for slightly weathered oil (Wang and Fingas, 1995).

**TABLE 1** shows the distribution of the peaks and their retention time monitored in 13 different m/z groups used in this study.



**FIG. 2-** Extracted ion chromatograms (m/z 113) showing heptanes, pristane, octadecane and phytane.

**TABLE 1-** Selected peaks at different m/z and their retention times

Peak	RT	Peak	RT	Peak	RT	Peak	RT
113a	27.49	192a	31.05	206a	32.88	216c	37.62
113b	27.67	192b	31.15	206b	33.71	216d	37.73
113c	29.58	192c	31.35	206c	34.06	220a	35.75
113d	29.79	192d	31.52	212a	32.24	220b	35.88
156a	20.58	192e	31.62	212b	32.52	220c	36.09
156b	20.66	198a	30.24	212c	32.61	220d	36.19
166	24.43	198b	30.54	212d	32.96	226a	33.90
170	23.72	198c	30.92	212e	33.09	226b	34.39
184a	26.57	202a	33.71	216a	36.77	226c	34.99
184b	27.90	202b	35.06	216b	37.21	226d	35.23
						226e	35.31

To make the data comparable between samples, the peak height of each ion from extracted ion chromatograms of a diesel sample was normalised to the peak height of 2,3,5-trimethylphenanthrene monitored at m/z 220. The peak is denoted as 220b in **FIG. 3**. This compound was thought to be a

good candidate because it has a relatively height molecular weight (higher retention time), thus is more likely to be resistant to evaporative weathering (such as in the case of a spill). In addition, this peak is well defined and has a reasonable intensity in most of the samples. In

crude oil samples, peaks such as this are suggested for normalization since the n-alkanes are subjected

to biodegradation over extended periods (Millner *et al.*, 1992).

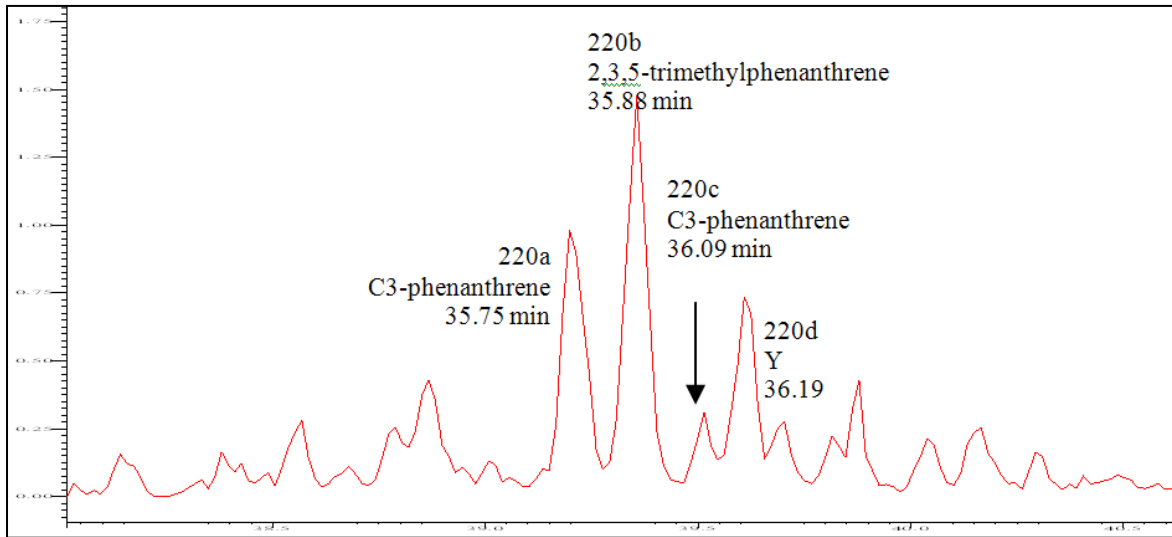


FIG. 3- Extracted ion chromatogram showing peaks of m/z 220 and their retention times.

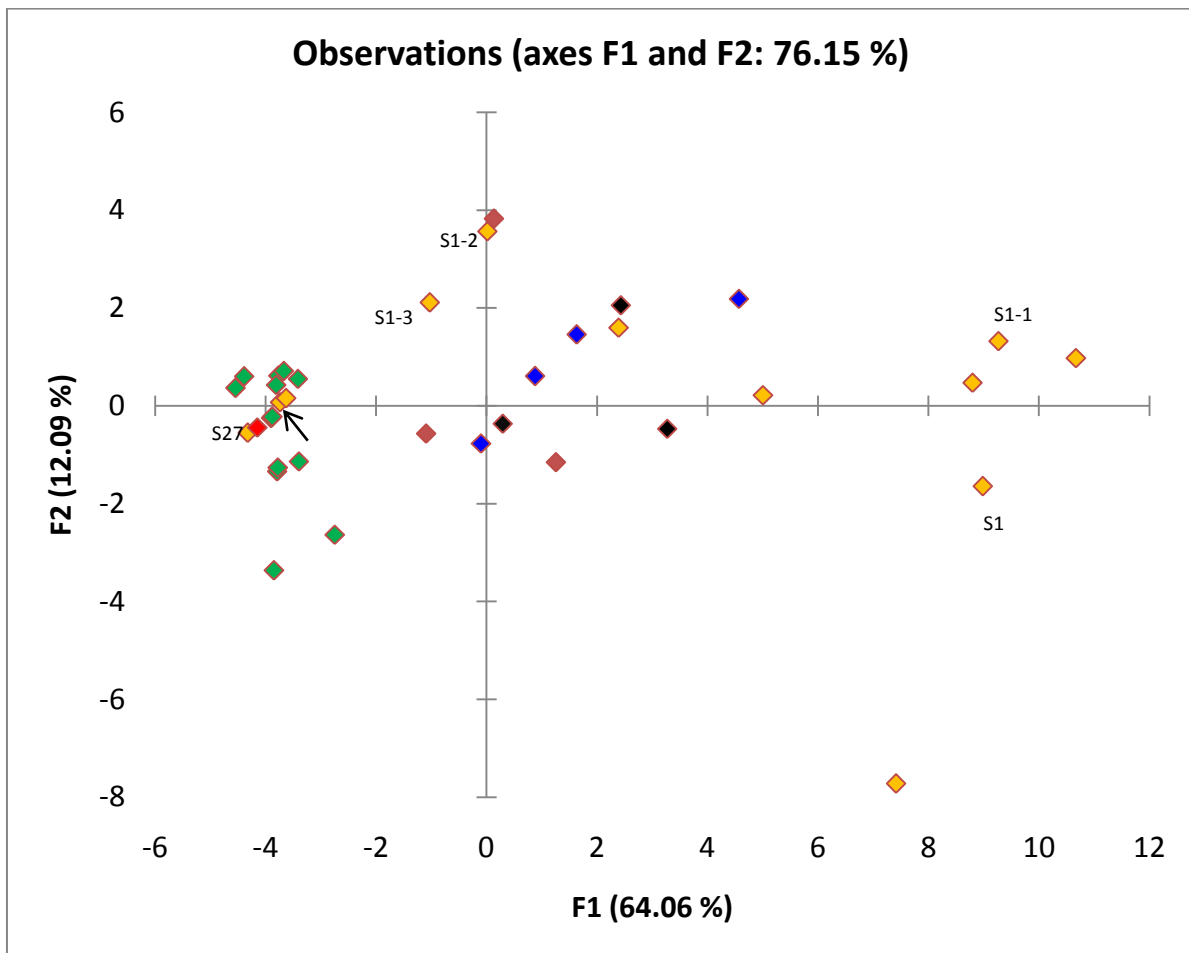


FIG. 4- Sore plot of PC<sub>1</sub> and PC<sub>2</sub> of diesel samples

Keys: Green =Petronas Diesels, Yellow=Shell diesels, Blue=Caltex Diesel, Brown=Mobil diesels, Black=Esso Diesels, S1-Shell service station 1; S1-1, S1-2 and S1-3 – Samples collected from Shell Service station 1 after 1, 2 and 3 weeks, respectively, Red (BLT)=sample for blind test.

**FIG. 4** shows the score plots for the first and second principal components for data derived from GC-MS chromatograms of diesels using principal component analysis. The original datasets contained peak height information for 41 peaks from each chromatogram, normalised to m/z 220b, **FIG. 3**, and log-transformed. Principal component 1 and principal component 2 accounted for 64.06% and 12.09% of the total variance between the samples, respectively.

Examination of the score plots reveals that Petronas diesel samples (green) were tightly clustered at the left of the score plot indicating similarities among the samples. This can be explained if the same source of petroleum from the refinery was refined or distributed to the service stations. Note that Petronas (the national petroleum company in Malaysia) produces and refines its products in Kerteh, Terengganu and this may explain the close proximity of most Petronas samples on the score plot.

Shell samples (yellow) were most widely scattered, except for a pair appeared close to Petronas samples (arrow), implying that diesel fuels from a given brand can be greatly different, depending on the batch of diesel used as well as how fast the supply from a given batch is consumed.

Mobil (brown), Esso (black) and Caltex (blue) diesel samples were also loosely cluster in the centre of the plot. Note that Mobil and Esso could also have sourced their diesel from the same supplier but the score plot shows that both Mobil and Esso diesels were greatly different based on the distance between each other on the score plot.

Three samples (S1-1, S1-2 and S1-3) collected from Shell service station (S1) at approximately one-week intervals on different days were grouped far away from sample S1 collected as part of one-day survey. This implies that these later three samples were significantly different from sample S1. Such variability is expected if this service station has received one or more new batches of diesel after S1 was collected.

A blind test as performed using one of the diesel samples with its service station unknown to the authors. The result (red) shows that the test sample was nearly overlapping with a Shell sample (labeled as S27), i.e. its original source indicating the test sample can be matched to its original known source, using our data treatment and statistical analysis.

## Conclusion

GC-MS data shows that there were similarity among samples from collected Petronas service station in Kota Bharu. Shell, Esso, Mobil and Caltex diesels collected on the same day were significantly different between service stations using GC-MS. Diesels collected from service stations on different occasions were also found to be differentiable upon PCA. Therefore, background information on the variability of diesel is important. Similarities between two samples upon statistical analysis may indicate they were from the same brand (such as seen in most of the Petronas samples). However, samples from different station of a same brand may be different greatly as seen in Shell diesels. The time interval between two samples collected from a service station can affect the diesel profiles.

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