

Evaluation of evidence value of car primer using pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) and chemometrics

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ABSTRACT

The car paint system consisted of four different layers; namely cathodic electrodeposition (CED), primer, the basecoat, and clear coat. Each of these layers may offer valuable information in an analysis of car paint. However, the recovery of a small amount of car paint from a crime scene may not consist of all four layers. Thus, this study is conducted to evaluate the evidence value of car primer in the presence of basecoat and absence of clear coat. In this study, 80 car paint samples, consisting of eight different red basecoats and ten types of primers were analyzed using Py-GC-MS to evaluate the contribution of the primer layer in the analysis of car paint sample. The chromatographic dataset obtained was subjected to chemometric techniques namely principal component analysis (PCA) and cluster analysis (CA). 22 principal components were rendered from PCA with a total variance of 81.23%. CA's three clusters are cluster 1 and 3 which was based on the shades of red basecoat while cluster 2 was based on the type of primer. This observation showed that the car primer might have a significant contribution to the analysis of car paint using Py-GC-MS.

Keywords: *Car primer, car paint analysis, Py-GC-MS, chemometric*

INTRODUCTION

Car paint analysis is one of the important analysis in the forensic laboratory for accidents or hit-and-run cases. The traces of car paint can be recovered either on the victim's car, on the human body, or at an accident scene. These car paint chips are valuable evidence as they can be used to identify the suspected car. The car paint system normally consists of four very thin layers. The bottom layer which is called cathodic electrodeposition (CED) functions to provide good adhesion to the car body as well as to the subsequent layers. On top of CED is the primer layer which gives mechanical strength to the coating and resistance against degradation by ultraviolet light, other than to provide a good even surface for maximum appearance and performance of the basecoat. The colour of the car body is given by the third layer which is the basecoat. The final coating is the clear coat, for the protection of the basecoat [1]. However, the metal and plastic parts of the car body may give different chemical structures and compositions as they are characterized by different adhesion and elasticity even though they have similar external colour [2].

In the examination of car paint samples, information on colour, morphology, and chemical composition are usually obtained from optical and spectrometric methods [3,4]. The most common spectrometric method used in car paint analysis is Fourier transform infrared spectroscopy (FTIR). FTIR analysis is commonly used in car paint analysis as it is sensitive to molecular structure and therefore provides much information about the chemical composition of a paint sample [5]. However, if only a small amount of sample is recovered, identification of the organic pigments using FTIR is almost impossible, thus reducing its discriminating power [5]. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has gained interest in a forensic investigation as it can be applied for trace analysis. Moreover, it has high discriminating power especially if the samples have slightly similar chemical compositions [6]. This method has been applied to differentiate types of binders of paint coatings [3] and clearcoat of car paint [7]. A study by Burns [8] showed that Py-GC-MS was able to discriminate paint samples that were indistinguishable using FTIR analysis. In our previous study, Py-GC-MS have shown its ability in discriminating different types of car primer [9]. These studies have shown the ability of the Py-GC-MS method in discriminating different types of car paint samples.

The chemometric technique has been used to analyze large and complex dataset as it can provide accurate and significant results in a short time [10]. Principal component analysis (PCA) is a commonly used chemometric technique. The analysis provides significant variables based on a linear combination of the original variables and provides interrelationship between samples and variables [11,12]. Cluster analysis (CA) is another chemometric technique used for grouping of samples based on the similarities of variables. The samples with the most likely measured variables will be grouped in the same cluster [10,13]. Chemometric techniques have been widely used for the discrimination and classification of samples such as in the analysis of car paint [14], household paint [15], spray paint [16], ballpoint inks [17], inkjet inks [11], and red lipsticks [18].

Many studies have been conducted based on the two top layers of the car paint system which is the clear coat or the basecoat. These two layers have shown their efficiency in the analysis of car paint samples. However, there are possibilities that any of these layers were absence in the car paint samples. Thus, analysis of the bottom layer which is the primer layer should be conducted. Therefore, this study aims to evaluate the evidence value of car primer in car paint analysis. In this study, 80 car paint samples consisted of eight different red base coat with ten different car primer were analysed using Py-GC-MS. Chemometric techniques were applied into Py-GC-MS dataset to discriminate the car paint samples and evaluate the contribution of car primer in the forensic analysis of car paint.

EXPERIMENTAL

Materials

Ten different types of car primer (label 01 to 10) and eight different shades of red basecoat (label A to H) of different brands were obtained from several local workshops around Shah Alam, Malaysia. The aluminum sheet (as the base) was purchased from the local hardware shop.

Procedure

Each of ten car primer (01 to 10) were mixed with a hardener before being applied on the aluminum sheet (5cm x 5cm) and baked in the oven at 60 °C for 30 minutes. After completely dry, the car primer chips were coated with every eight red basecoats (A to H) and were baked at 60 °C for 30 mins. These car paint samples were allowed for completely aging at room temperature for at least three days. The total of car paint samples prepared was 80 samples. The list of the car paint samples used in this study was as tabulated in Table 1.

Table 1: List of car paint samples

Red basecoat	Sample Code	Total samples (n = 10)
A	A01..... A10	10
B	B01..... B10	10
C	C01..... C10	10
D	D01..... D10	10
E	E01..... E10	10
F	F01..... F10	10
G	G01..... G10	10
H	H01..... H10	10

Note: Sample code A01 refers to A type red basecoat with the first type of car primer and so on.

Instrumentation

The red basecoats were analyzed using video spectral comparator (VSC 5000, Foster and Freeman, UK) based on CIE system (International Commission on Illumination, Vienna) which expressed as L^* (lightness), a^* (redness/greenness), and b^* (yellowness/blueness). Each of the samples was analysed at least three times at various spots. The paint samples were analyzed using PY-2020iD pyrolyzer attached to Agilent Technologies 7890A gas chromatography coupled with Agilent Technologies 5975C mass spectrometer. The sample (0.3 – 0.5 mg) was placed inside a quartz tube held in the platinum coil of the pyroprobe and introduced into the pyrolyzer. Pyrolysis was performed at a temperature of 750 °C for 6 s with an interface temperature of 350 °C. The products of pyrolysis were separated on a 5% phenylpolysiloxane and 95 % methylpolysiloxane capillary column (30 m x 0.25 mm x 0.25 μ m) in the gas chromatography (GC). The GC parameter was set at 40 °C for 3 mins, ramped at 10 °C/min to the temperature of 280 °C, and held for 20 mins. Helium was used as the carrier gas with a pressure of 70kPa. Elution times for all compounds were obtained within 30 mins. A mass spectrometry detector was used in electron ionization mode at 70 eV. The compounds were identified using NIST08 MS library search with quality matching above 80%. The analysis was done at least three times for each sample.

Chemometric analysis of Py-GC-MS dataset

The dataset of the pyrolysis products was subjected to PCA and CA using XLSTAT2014 software.

RESULTS AND DISCUSSION

Video Spectral Comparator (VSC)

Examination of the colour of car paint samples is the common approach in car paint analysis. Even though the colour of the car paint samples can be examined visually, the microspectrophotometry method is more practical as sometimes examination of the small size of car paint samples could be tricky. The ability of this method has been used in discriminating car paint colour of the different and same colour [3,15]. Thus, the examination of the red basecoat used in this study was conducted using VSC to confirm the different shades of the red colour used.

Table 2 shows the colorimetric dataset of red basecoat obtained from VSC examination expressed as luminosity value (L), degree of redness (a^*), and degree of yellowness (b^*). The results showed that each sample has different shades based on the L value. The lowest L value of 43.8 of sample B showed that this sample gave the darkest red shade. The lightest red basecoat was sample G with an L value of 63.4. Each sample also has a different intensity of red colour as

the different values of a^* were recorded. The samples with a more positive value of a^* showed that they are having a more intense red colour.

Table 2: Colorimetric data for red basecoat

Red Basecoat	L	a^*	b^*
A	57.2	69.4	28.2
B	43.8	42.5	3.0
C	60.2	67.2	31.3
D	62.0	45.5	10.0
E	50.0	67.1	18.6
F	44.1	47.2	4.2
G	63.4	68.7	34.1
H	48.5	51.0	13.7

The differences between the colours of two red basecoats (ΔE) can be determined through a three-dimensional application of Pythagoras's theorem (equation 1) as had been used in previous studies [16,17].

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2} \quad (1)$$

Where L_1, a_1, b_1 and L_2, a_2, b_2 are the CIELAB values obtained for two compared samples. The ΔE value obtained for red basecoats is shown in Table 3. Zieba-Palus [21] stated that the two colours were different from each other if the ΔE value is larger than 10. The ΔE value obtained by most of the red basecoats was larger than 10 except for sample differentiation between red basecoat A-C, A-G, B-F, and C-G. However, another study by Trzcińska [19] reported that two samples were different from each other if the ΔE value is greater than 3. Therefore, in this study, all eight red basecoats used having a different lightness and chroma value.

Table 3: ΔE values obtained by red basecoat

Red Basecoat	A	B	C	D	E	F	G	H
A	0.00	39.2	4.81	30.4	12.2	35.2	8.59	24.9
B	39.2	0.00	41.0	19.7	29.7	4.81	45.1	14.5
C	4.81	41.0	0.00	30.5	16.3	37.3	4.50	26.6
D	30.4	19.7	30.5	0.00	26.1	18.9	33.4	15.0
E	12.2	29.7	16.3	26.1	0.00	25.2	20.5	16.8
F	35.2	4.81	37.3	18.9	25.2	0.00	41.5	11.1
G	8.59	45.1	4.50	33.4	20.5	41.5	0.00	30.8
H	24.9	14.5	26.6	15.0	16.8	11.1	30.8	0.00

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Figure 1 shows the representative pyrograms from four red car paint samples. Pyrograms 1a and 1b were from samples of the same car primer (primer 02) with different red basecoat (D and F, respectively). Meanwhile, pyrograms 1c and 1d were from samples having the same basecoat (basecoat A) with different car primer (06 and 10, respectively). It can be seen that there were similarities and dissimilarities among the pyrograms which correspond to the product of degradation of the polymer and its monomer. In general, similar patterns were observed for the first 15 mins of analysis. As the pyrograms obtained were complex, the relative intensities of selected important compounds were based on the highest peak in the pyrograms [22].

The analysis was based on the method suggested by Zieba-Palus [23]. The baseline of the pyrogram was shifted to the level of 10 % of the largest peak height and the visible peaks with relative height larger than 10 % were marked with 'strong'. The baseline was then downshifted to the level of 5 % of the largest peak height and the new peaks that appeared on the pyrogram were marked with 'moderate'. Consequently, 'weak' was given for the compounds with relative peak height in a range from 2 to 5%. Compounds with relative peak height less than 2 % were marked with 'x' as these peaks were very small and inconsistent. Selected compounds identified in the pyrograms of selected red car paint samples are listed in Table 4.

The common compounds identified in the red car paint samples include α -methylstyrene, indene, naphthalene, and 2-methylindene. All these compounds were observed as major compounds in the pyrograms as they were marked as 'S'. Ethylbenzene was the major compound

in red car paint sample of the same car primer (D02 and F02) but it was identified as minor in samples of other car primers (A06 and A10). The same result was observed for (E)-stilbene. All of these compounds might be from the degradation of the car primer [9]. Therefore, discrimination of the red car paint samples based on the major compounds only was impossible as they were observed in almost red car paint samples. Thus, the minor peaks which correlated to minor compounds may be used to discriminate or differentiate the samples [23].

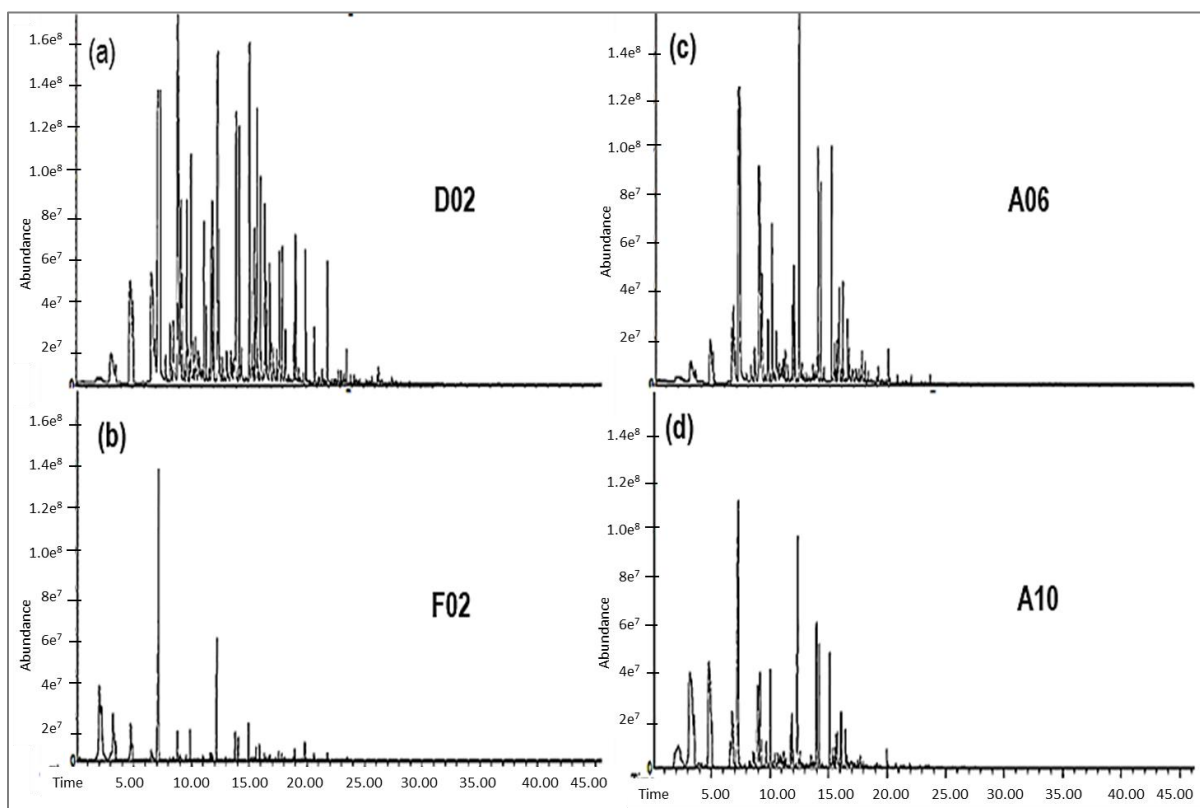


Figure 1: Pyrograms of different red car paint samples

The dissimilarities of the pyrograms were observed after 20 mins because of the minor compounds in the pyrograms (marked with 'W' or 'x'). 1-naphthalenecarbonitrile, N-allylphthalimide, and 2-phenyl-benzoxazole were identified as minor compounds in the samples of different car primer varieties (A06 and A10) but were not observed in the samples of the same car primer (D02 and F02). These compounds could be the pyrolysis products of the red basecoat. Thus, these minor compounds may also be used in discriminating against the red car paint samples.

Table 4: Selected compounds identified from Py-GC-MS analysis

Retention time	Compound	Label	A06	A10	D02	F02
4.32	Pyridine	C1			W	
4.44	Cyclopentanone	C2		W		
6.58	Ethylbenzene	C3	S	S	W	M
6.88	Phenylethyne	C4	M	x		
7.18	Styrene	C5	S	M		
7.34	1,3,7-Octatrien-5-yne	C6		S		
7.44	Benzenemethanimine	C7				
8.56	Benzaldehyde	C8				
8.91	α -methylstyrene	C9	S	S	S	
8.96	Benzonitrile	C10		S		S
9.21	m-Aminophenylacetylene	C11				
9.55	cis- β -methylstyrene	C12				W
9.89	Indane	C13	S		W	
10.1	Indene	C14	S	S	S	S
10.4	Acetophenone	C15				
10.5	Triquinacene	C16				
10.67	o-Isopropenyltoluene	C17		W	M	
10.9	Benzoic acid, methyl ester	C18				
11.0	3-Phenyl-2-propyn-1-ol	C19				
11.0	2-methyl-benzoxazole	C20				
11.5	Indolizine	C21			x	
11.6	Benzyl nitrile	C22				
11.8	2-Methylindene	C23	S		S	M
11.9	Naphthalene	C24	S	S	S	
12.00	1-(4-methylphenyl)-ethanone	C25				
12.1	1,4-Dihydronaphthalene	C26	S		S	
12.4	Azulene	C27	S		S	
12.6	3-(4-methylphenyl)-2-propyn-1-ol	C28			M	
13.1	Quinoline	C29	W		M	W
13.5	Isoquinoline	C30			W	
13.8	Benzocycloheptatriene	C31		W		x
14.5	2,5-dichloro-benzenamine	C32				
15.1	Acenaphthene	C33				
16.1	Biphenylene	C34	M	M		M

Table 4 continued:

Retention time	Compound	Label	A06	A10	D02	F02
16.6	1-Naphthalenecarbonitrile	C35	M	W		x
16.8	1,1-diphenyl-ethylene	C36				
16.8	4a,9a-Methano-9H-fluorene	C37				
16.9	Dibenzofuran	C38				
16.9	cis-Stilbene	C39	M		W	
17.2	1(2H)-Acenaphthylenone	C40				
17.3	N-Allylphthalimide	C41	W	W		
17.5	2-Fluorencarboxaldehyde	C42				
17.5	1H-Phenylene	C43				
17.5	4-Ethylbiphenyl	C44				
17.7	Fluorene	C45	S	W	W	W
18.2	Benzophenone	C46				
18.6	2-Hydroxyfluorene	C47		W		
18.7	[1,1'-biphenyl]-4-carboxaldehyde	C48				
19.1	(E)-Stilbene	C49	S	M	W	x
19.3	1,2-Diphenylcyclopropane	C50				
19.5	9H-Fluoren-9-one	C51	x	x	x	
19.7	6(5H)-Phenanthridinone	C52				
19.7	2-phenyl-benzoxazole	C53	M	W		
19.9	Diphenylethyne	C54				
20.8	Dibenzo[a,e]cyclooctene	C55		W		
21.0	Naphtho[2,3-b]norbornadiene	C56				
21.1	o-Terphenyl	C57	x			
21.2	Methyl ester hexadecanoic acid	C58	W			
21.3	5H-Dibenzo[a,d]cycloheptene	C59				
22.1	5,6-dihydro-4H-benz[de]anthracene	C60				
22.8	Fluoranthene	C61	x	x	x	
23.5	Indeno[2,1-b]chromene	C62				
23.5	p-Terphenyl	C63	W			
23.6	Benzo[b]naphtho[2,3-d]furan	C64		x		
23.9	m-Terphenyl	C65	x			
24.0	Benzo[kl]xanthene	C66			W	
24.2	11H-Benzo[a]fluorene	C67	x		x	
24.5	5'-methyl-1,1':3',1''-Terphenyl	C68	x			

Table 4 continued:

Retention time	Compound	Label	A06	A10	D02	F02
25.7	Benzo[c]phenanthrene	C69				
26.2	Benz[a]anthracene	C70				
26.3	Triphenylene	C71			x	

Note: S – strong (above 10 %), M – moderate (5 -10 %), W – weak (2-5 %), x – below 2 %

Principal Component Analysis (PCA)

The complex and large dataset from Py-GC-MS analysis was subjected to principal component analysis (PCA). PCA of the red car paint samples revealed 81.23 % of the total variance from 22 principal components (PCs) with eigenvalue more than 1. The variance of PC1 and PC2 were responsible for 12.86 % and 9.20 % of the total variance, respectively. Figure 2 showed the score plot of PC1 and PC2.

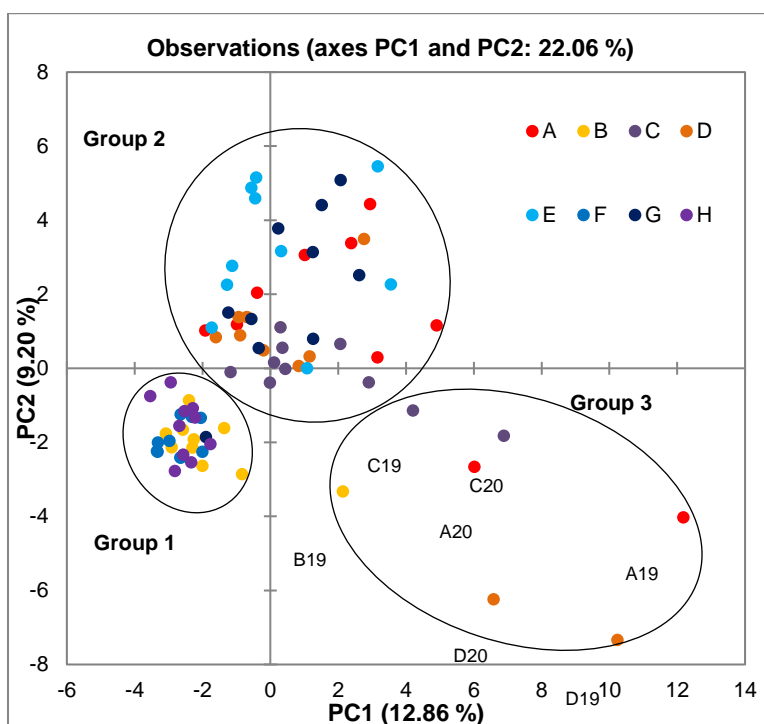


Figure 2: Score plot of PC1 and PC2 of the red car paint samples from Py-GC-MS data set

Three groups were obtained in the score plot of the car paint samples. Group 1 located at the negative axis of the score plot consisted of B, F, and H car paint samples. Group 2 belongs to A, C, D, E, and G was located at top of the positive axis of the score plot. Group 3 located at the bottom positive side of the score plot consisted of samples of various basecoats of two types of car primer. In general, samples in group 1 and group 2 consisted of several basecoats but include all types (10) of primer. This may suggest that the grouping was based on similarities of the compounds that made up the shades of the basecoats. Based on the VSC analysis, the samples in group 1 have L values within 43 to 48, while the samples in group 2 have higher L values of within 50 to 63. However, group 3 consisted of samples of four different basecoats but only two types of primer (primer 04 and 05). As reported in our previous study [7], these two primers were from 2k types having similar compounds. Thus, it can be concluded that group 3 is based on the type of primer.

Figure 3 shows the loading plot, suggesting the compounds responsible for the distribution of the samples in the score plot. The further away from the compounds from the plot origin, the stronger impact that variable has on the model [24]. PC coefficients correlating greater than 0.75, between 0.75 and 0.50, and between 0.50 and 0.30 are considered to have “strong”, “moderate”, and “weak” significant factor loading, each respectively [25].

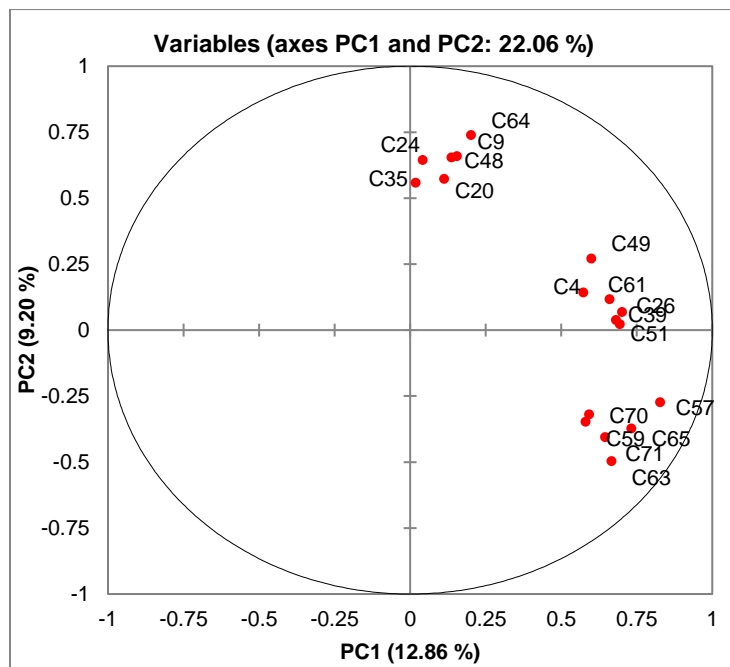


Figure 3: PCA loading plot of PC1 and PC2 of the red car paint from Py-GC-MS data sets

The compounds in the loading plot are listed in Table 4. In PC1, C57 (o-terphenyl) has strong factor loading while compounds with moderate factor loading include C4 (phenylethyne), C26 (1,4-dihydronaphthalene), C39 (cis-stilbene), C49 (E)-stilbene), C51 (9H-fluoren-9-one), C59 (5H-dibenzo[a,d]cycloheptene), C61 (fluoranthene), C63 (p-terphenyl), C65 (m-terphenyl), C70 (benz[a]anthracene), and C71 (triphenylene). All of these were observed as minor compounds in the pyrograms except 1,4-dihydrohaphthalene and (E)-stilbene. Most of these compounds were observed in the pyrolysis products of car primer [9]. Since group 3 was located on the positive side of PC1 (Figure 2), it is positively affected by these compounds. Therefore, compounds from the car primer may give a significant contribution to the grouping of the score plot. This observation showed that the minor compounds were responsible for the discrimination of the samples as suggested by Zieba-Palus [20].

As for PC2, no compound was observed with high factor loading while several compounds were categorized with moderate factor loading. The compounds with moderate factor loading include C9 (α -methylstyrene), C20 (2-methylbenzoxazole), C24 (naphthalene), C35 (1-naphthalenecarbonitrile), C48 ([1,1'-biphenyl]-4-carboxaldehyde) and C64 (benzo[b]naphtho[2,3-d]furan). α -methylstyrene and naphthalene were observed in both car primer [9] and red basecoat pyrograms. However, the other four compounds (2-methylbenzoxazole, 1-naphthalenecarbonitrile, [1,1'-biphenyl]-4-carboxaldehyde and benzo[b]naphtho[2,3-d]furan) were only observed in the red basecoat. As observed in the score plot (Figure 2), discrimination of group 1 and group 2 may be due to the compounds from the basecoats.

Cluster Analysis

The Py-GC-MS dataset of 80 red car paint samples was subjected to cluster analysis (CA). Clustering of the samples in CA was based on the natural grouping that could occur based on the similarity or dissimilarity of the compounds detected in the samples as shown in Figure 4. There were three main clusters were observed in the dendrogram. Car paint samples consisted of A, C, D, E, and G red basecoat was grouped together in cluster 1. However, in cluster 2 there were samples A03, A04, A05, A06, C02, C04, C05, D01, D02, D04, D05, and D06. The rest of the samples (B, F, and H) were grouped in cluster 3. The samples in cluster 3 were most different from samples in clusters 1 and 2 as they were separated into the individual leg. Cluster 1 and 2 which were subdivided from the same dendrogram leg consisted of similar basecoat. Cluster 1 consisted of samples having the same basecoat and samples in cluster 2 were grouped based on their car primer varieties. Both PCA and CA analysis complement each other as both approaches resulted in three distinct groups or clusters. Two groups or clusters consisted of red car paint samples of similar shades of basecoat and another group or cluster consisted of samples having similar car primer.

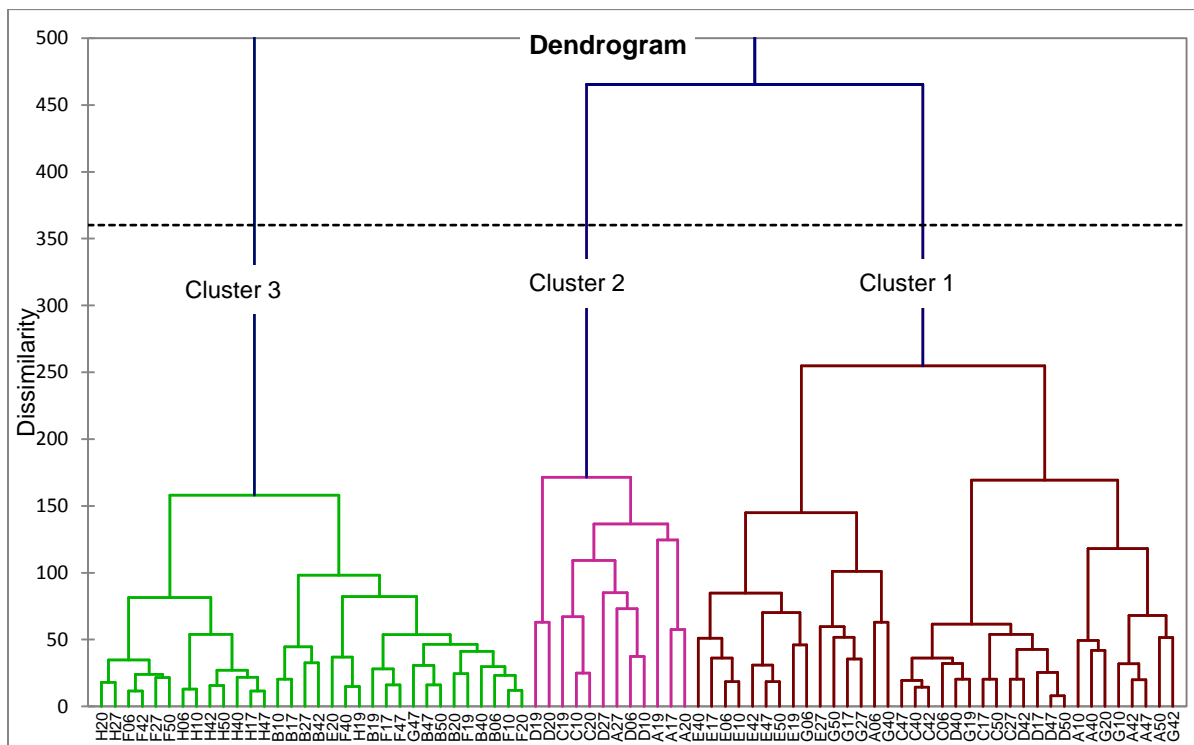


Figure 4: Dendrogram of clustering of car paint from Py-GC-MS dataset

CONCLUSION

Different shades of the same basecoat colour can be confirmed by the micro-spectrophotometry method using VSC. Py-GC-MS method was able to analyze car paint samples containing both car primer and basecoat without separation of each layer before analysis. Results obtained from PCA identified the compounds from car primer were responsible for the groupings obtained in the PCA score plot. CA dendrogram revealed one cluster containing samples of the same car primer. This observation showed the car primer might have a significant contribution in car paint analysis using Py-GC-MS.

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