# Classification of Car Paint Primers Using Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) and Chemometric Techniques

**Raja Zubaidah Raja Sabaradin[1], Norashikin Saim[1]\*, Rozita Osman[1] and Hafizan Juahir[2]**

[1]*Faculty of Applied Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[2]*East Coast Environmental Research Institute, Universiti Sultan Zainal Abidin (UNISZA),*
*21300 Gong Badak Campus, Kuala Terengganu, Malaysia*

## ABSTRACT

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has been recognised as an effective technique to analyse car paint. This study was conducted to assess the combination of Py-GC-MS and chemometric techniques to classify car paint primer, the inner layer of car paint system. Fifty car paint primer samples from various manufacturers were analysed using Py-GC-MS, and data set of identified pyrolysis products was subjected to principal component analysis (PCA) and discriminant analysis (DA). The PCA rendered 16 principal components with 86.33% of the total variance. The DA was useful to classify the car paint primer samples according to their types (1k and 2k primer) with 100% correct classification in the test set for all three modes (standard, stepwise forward and stepwise backward). Three compounds, indolizine, 1,3-benzenedicarbonitrile and p-terphenyl, were the most significant compounds in discriminating the car paint primer samples.

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

## INTRODUCTION

Automotive paint analysis is one of the important analyses in the forensic laboratory for accidents or hit-and-run cases. Generally, traces of automotive paint can be recovered either from the victim's car, human body or at the scene of the accident. These automotive paint chips are valuable evidence as they can be linked to the vehicles involved. The paint

finish normally consists of four very thin layers, namely cathodic electro deposition (CED), primer, basecoat and clearcoat.

In examining car paint, the optical and spectrometric methods are commonly used in order to obtain information about its colour, morphology and chemical composition (Trzcińska, Zięba-Palus, & Kościelniak, 2009; Zięba-Palus, Michalska, & Wesełucha-Birczyn, 2008). Fourier transform infrared spectroscopy (FTIR) is the most common spectrometric method used in car paint analysis. This method is sensitive to molecular structure and therefore provides much information about the chemical composition of a paint sample. However, if a small amount of sample is recovered, identification of the organic pigments using FTIR is almost impossible, thus reducing its discriminating power (Zięba-Palus et al., 2011).

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) has gained interest in forensic investigation as it can be applied for trace analysis. This method has been applied to differentiate types of binders of paint coatings (Zięba-Palus, Zadora, & Milczarek, 2008) and clear coat of car paint (Plage, Berg, & Luhn, 2008). Burns and Doolan (2005) showed that Py-GC-MS was able to discriminate paint samples indistinguishable using FTIR analysis.

The chemometric techniques with spectroscopic data produce efficient, rapid and more robust outcome than a classical visual comparison (Muehlethaler, Massonnet, & Esseiva, 2011). This technique has been widely used to discriminate and classify the samples. This method is efficient in exploring and analysing spectroscopic data sets. It has been applied in the analysis of household paint (Muehlethaler et al., 2011), spray paint (Muehlethaler, Massonnet, & Esseiva, 2014), ballpoint inks (Borba, de Honorato, & de Juan, 2015), and inkjet inks (Gál, Oravec, Gemeiner, & Čeppan, 2015).

In this study, car paint primer samples from various manufacturers were analysed using Py-GC-MS. This study used two types of car paint primer, 1k and 2k types. The 1k car paint primer refers to the "one component" paint which does not require hardener and can be directly applied on the surface, while the 2k car paint primer is a "two-component" paint mixed with hardener at certain ratio before it can be applied on the surface. Otherwise, the car paint primer will not harden on the surface. Chemometric techniques have been used to evaluate the potential of Py-GC-MS data of car paint primers in forensic investigation.

## MATERIALS AND METHOD

Car paint primer samples, as listed in Table 1, were obtained from workshops in Selangor, Malaysia. The 1k car paint primer samples were directly applied on the aluminium sheet and baked for 20 minutes at 120°C. The 2k primer samples were prepared by mixing them with the hardener and applied on the aluminium sheet before they were baked in the oven at 60°C for 30 minutes. The car paint primer sheet was polymerised for at least three days. The samples were scrapped off using a utility knife prior to analysis.

Table 1
*List of samples*

| Car primer type | Sample |
| --- | --- |
| 1k | P001 – P005 (5 samples) |
| 2k | P006 – P050 (45 samples) |

Te Py-GC-MS analysis was conducted using a PY-2020iD pyrolizer attached to Agilent Technologies 7890A gas chromatograph coupled with Agilent Technologies 5975C mass spectrometer. All samples were weighed prior to the analysis (0.3 mg). The samples were then placed inside a quartz tube held in the platinum coil of pyroprobe. The pyrolysis was performed at the temperature of 750°C for 6 seconds with interface of 350°C. The product of the pyrolysis was then transferred to the chromatographic capillary column (30 m x 0.25 mm, 0.25 m) for separation. The stationary phase of the gas chromatography (GC) column consisted of 5% diphenylpolysiloxane and 95% dimethylpolysiloxane. The GC parameter was set at 40°C for 30 minutes, ramped at 10°C/min at 280°C for 20 minutes. Elution times for all compounds were obtained within 30 minutes. The analysis was run at least three times for each sample. The compounds were identified using NIST08 MS library search with quality matching more than 80%.

Py-GC-MS data set is large and has complex information. The data set of pyrolysis products was subjected to chemometric techniques (principal component analysis (PCA) and discriminant analysis (DA) to display the most significant patterns and possible groupings and sources of data variation. In this study, XLSTAT2014 software was used for the multivariate statistical calculations.

The PCA is an exploratory, multivariate, statistical technique that can be used to examine data variability. This technique provides information on the most meaningful parameters that describe the whole data set rendering data reduction with minimum loss of the original information (Vega, Pardo, Barrado, & Deban, 1998). The PCA was applied on the data set from the Py-GC-MS to identify and determine the sources of car paint primer compounds.

The DA determines the variables that discriminate between two or more naturally occurring groups/clusters. It constructs a discriminant function (DF) for each group (Singh, Malik, Mohan, Sinha, & Singh, 2004, 2005). The DFs were calculated using equation (1)

$$f(G_i) = k_i + \sum_{j=1}^{n} w_{ij} P_{ij} \tag{1}$$

Where $i$ is the number of groups (G), $k_i$ the constant inherent to each group, $n$ the number of parameters used to classify a set of data into a given group and $w_j$ is the weight coefficient assigned via DF analysis (DFA) to a given parameter ($p_j$). In this study, DA was applied to the pyrolysis products using the standard, forward stepwise and backward stepwise modes. In the forward stepwise mode, variables were included step-by-step beginning from the most significant variables until no significant changes were seen. In backward stepwise mode,

variables were removed step-by-step beginning with the less significant variables until no significant changes were noted. The DA may help in identifying the significant compounds for classification of the car primer according to their types.

## RESULTS AND DISCUSSION

Figure 1 shows selected pyrograms of two different types of car paint primer, 1k (P003 and P004) and 2k (P021 and P024). The patterns of these pyrograms correspond with the product of degradation of the polymer and its monomer. Similar patterns were observed in the first 15 minutes. However, after 15 minutes of analysis, some differences in the patterns of the pyrograms showed the potential of Py-GC-MS in differentiating the car paint primer samples. Milczarek, Zięba-Palus and Kościelniak (2005) found the relative intensities of some important compounds may be used based on the highest observed peak in the pyrograms. In this study, two compounds, styrene (7.15 minutes) and azulene (12.35 minutes) were selected.
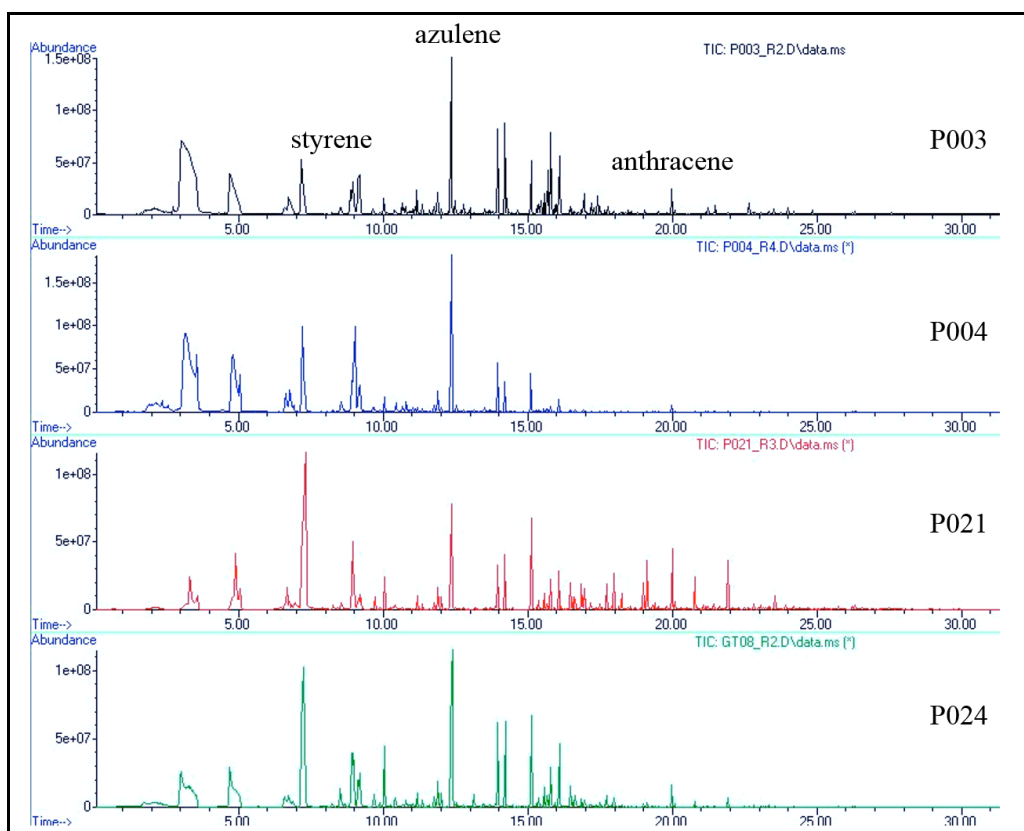


*Figure 1.* Pyrograms of car paint primer of different types

Evaluating the discriminating ability of pyrograms for car paint primer samples was based on the procedure recommended by Zięba-Palus, Michalska, Wesełucha-Birczyn and Kościelniak (2008). The baseline of the pyrogram was shifted to the level of 10% of largest peak height. Visible peaks with relative height larger than 10% were marked with 'A'. Similarly, when the baseline was downshifted to the level of 5% of largest peak height, new peaks that appeared on the pyrogram were marked with 'B'. Consequently, 'C' was given for the compounds with signals of relative height in range from 2 to 5%. Peaks with relative height less than 2% were marked with 'ND' as these peaks were very small and their reproducibility considered as inconsistent. Compounds identified in pyrograms of the selected car paint primer samples are listed in Table 2.

Common compounds in these primer samples include toluene, ethylbenzene, styrene, α-methylstyrene, indene, naphthalene and azulene with retention time of 4.70, 6.60, 7.15, 8.90, 10.00, 11.90 and 12.35 respectively. Toluene, ethylbenzene, α-methylstyrene, and naphthalene are the products of degradation of the polystyrene, a basic component of car paint primer. Azulene was the major compound (marked as 'A') present in all samples except P019 and P025. Thus, differentiating the car paint primer based on the compounds of level 'A' and 'B' was not possible as these compounds were observed in all samples.

Most compounds identified after 20 minutes of the analysis were minor compounds (marked as 'C' or 'ND'). Anthracene (20 minutes) was observed in almost all car paint primer samples. Some minor compounds, such as indolizine, were observed only in sample P005, triphenylmethane in sample P002 and di-p-tolylacetylene in sample P003. Sample P041 can be distinguished from other samples due to the presence of 3-methyl-methyl ester benzoic acid, (1-methylenebut-2-enyl) benzene, (Z)-7-hexadecene, methyl ester hexadecenoic acid, n-hexadecenoic acid. These compounds are most probably products of degradation of the main components. Thus, these minor compounds may be used in discriminating the car paint primer samples.

The PCA applied to the data set of 65 pyrolysis products resulted in 16 varifactors (VFs) explaining 86.33% of total variance. The PCs generated by PCA are sometimes not readily interpreted. Therefore, it is advisable to rotate the PCs by Varimax rotation. Varimax rotations applied on the PCs with eigenvalues greater than 1 are considered significant (Kim & Mueller, 1987) in obtaining new groups of variables called Varimax factors (VFs). The VF coefficients have a correlation 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 respectively (Liu, Lin, & Kuo, 2003). Table 3 shows the factor loadings after Varimax rotation.

Table 2

*Compounds identified in pyrograms of selected car paint primer of different manufacturers*

| Library ID | P001 | P002 | ... | P050 |
|---|---|---|---|---|
| Benzene | | | | |
| Pyridine | | | | |
| Toluene | | | | |
| Picolinyl 7,13,16-docosatrienoate | | | | |
| Ethylbenzene | | | | |
| o-Xylene | | | | |
| Phenylethyne | | | | |
| Styrene | | | | |
| Benzenemethanimine | | | | |
| Benzaldehyde | | | | |
| Phenol | | | | |
| alpha-Methylstyrene | | | | |
| Benzonitrile | | | | |
| Indane | | | | |
| Indene | | | | |
| Acetophenone | | | | |
| o-Isopropenyltoluene | | | | |
| Cinnamaldehyde, (E)- | | | | |
| Indolizine | | | | |
| Benzyl nitrile | | | | |
| 2-Methylindene | | | | |
| Naphthalene | | | | |
| 1,4-Dihydronaphthalene | | | | |
| Azulene | | | | |
| Benzo[b]thiophene | | | | |
| Benzoic acid, 3-methyl-, methyl ester | | | | |
| [1-Methylethenyl]-2-ethylbenzene | | | | |
| 1-Naphthalenol | | | | |
| Quinoline | | | | |
| Isoquinoline | | | | |
| 1,3-Benzenedicarbonitrile | | | | |
| Benzocycloheptaphene | | | | |
| Diphenylmethane | | | | |
| Biphenylene | | | | |
| 9-Octadecene, (E)- | | | | |
| Dibenzofuran | | | | |
| cis-Stilbene | | | | |
| 1(2H)-Acenaphthylenone | | | | |
| N-Allylphthalimide | | | | |
| 1H-Phenalene | | | | |
| 4-Ethylbiphenyl | | | | |
| Thioxanthene, (Z)- | | | | |
| Fluorene | | | | |
| Benzophenone | | | | |
| Benzo[h]quinoline | | | | |
| Phenanthridine | | | | |
| (E)-Stilbene | | | | |
| 9H-Fluoren-9-one | | | | |
| Phenanthrene | | | | |
| Anthracene | | | | |
| Dibenzo[a,e]cyclooctene | | | | |
| o-Terphenyl | | | | |
| Hexadecanoic acid, methyl ester | | | | |
| n-Hexadecanoic acid | | | | |
| Triphenylmethane | | | | |
| di-p-Tolylacetylene | | | | |
| Fluoranthene | | | | |
| Octadecanoic acid, methyl ester | | | | |
| Pyrene | | | | |
| p-Terphenyl | | | | |
| m-Terphenyl | | | | |
| Benzo[b]fluoranthene | | | | |
| Benzo[j]fluoranthene | | | | |
| Benzo[a]anthracene | | | | |
| Triphenylene | | | | |

There were five VFs associated with strong loading in the identification and determination of the sources of car primer compounds. The VF1 explained 18.33% of total variance with strong loading (>0.75) of cis-stilbene, (E)-stilbene, o-terphenyl, m-terphenyl, benzo(c) phenanthrene, benz(a)anthracene and triphenylene. This is the group of isomers with three different types of benzene arrangement. The stilbene and terphenyl isomers have two and three benzene rings respectively. The benzo(c)phenanthrene and benz(a)anthracene are the isomer of triphenylene with 4 benzene rings fused together. VF2 with 11.58% of the total variance has strong loading of (E)-cinnamaldehyde, 1,3-benzenedicarbonitrile, benzophenone, benzo(h) quinoline and phenanthridine. The strong loading in VF3 are 3-methyl-methyl ester benzoic acid, 1-methylenebut-2-enyl) benzene, (Z)-7-hexadecene, methyl ester hexadecanoic acid, n-hexadecanoic acid and methyl ester octadecanoic acid. The carboxylic acid is commonly found in car paint primer binder. Phenol, di-p-tolyacetylene and benzo(kl)xanthene are the dominant compounds in VF4. Phenol may be the product of degradation of the other main components in the car paint primer. The VF5 with relatively low variance (6.05%) has strong loading on naphthalene and 1,4-dihydronaphthalene which are the products of polystyrene degradation.

Discriminant analysis was applied to the raw data of pyrolysis products using standard, forward stepwise and backward stepwise modes. The standard, forward stepwise and backward stepwise modes yielded 100% correctly assigned based on 48, 3 and 47 compounds (Table 4 and Table 5) respectively. Forward stepwise DA shows that indolizine, 1,3-benzenedicarbonitrile and benzo[kl]xanthene are the discriminating compounds. Therefore, DA results suggested these were the most significant compounds in discriminating between the types of car paint primer.

Table 3
*Loading of car primer compounds on significant principal components for Py-GC-MS dataset*

| Compound | VF1 | VF2 | VF3 | VF4 | VF5 | VF6 | VF7 | VF8 | VF9 | VF10 | VF11 | VF12 | VF13 | VF14 | VF15 | VF16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pyridine | 0.010 | 0.038 | -0.025 | 0.067 | -0.134 | 0.050 | 0.076 | 0.032 | 0.024 | 0.134 | 0.047 | -0.007 | 0.934 | 0.013 | -0.014 | 0.007 |
| Toluene | 0.239 | 0.130 | 0.080 | 0.167 | -0.006 | 0.009 | 0.821 | -0.019 | -0.064 | 0.115 | 0.062 | 0.054 | 0.058 | -0.153 | -0.107 | -0.031 |
| Phenol | -0.082 | -0.070 | -0.025 | 0.915 | 0.060 | 0.052 | -0.021 | -0.009 | -0.026 | 0.147 | 0.063 | 0.015 | 0.100 | -0.078 | -0.056 | 0.020 |
| (E)-Cinnamaldehyde | 0.045 | 0.877 | -0.005 | -0.041 | 0.050 | -0.075 | -0.010 | 0.040 | 0.050 | 0.133 | 0.081 | -0.302 | -0.122 | -0.044 | -0.021 | 0.005 |
| Indolizine | -0.107 | -0.017 | -0.012 | -0.091 | -0.436 | -0.013 | 0.179 | -0.030 | -0.020 | 0.474 | -0.367 | -0.026 | 0.160 | -0.151 | 0.219 | -0.174 |
| Naphthalene | -0.139 | 0.103 | 0.081 | 0.076 | 0.849 | 0.098 | -0.043 | -0.148 | -0.011 | -0.080 | -0.023 | 0.025 | -0.010 | -0.025 | 0.051 | 0.019 |
| 1,4-Dihydronaphthalene | 0.209 | 0.140 | 0.035 | -0.014 | 0.842 | -0.036 | 0.218 | -0.021 | 0.026 | 0.147 | 0.059 | 0.004 | -0.095 | 0.091 | -0.001 | -0.085 |
| Azulene | -0.031 | 0.050 | 0.043 | 0.028 | -0.039 | -0.017 | -0.078 | -0.055 | -0.068 | 0.087 | -0.126 | 0.052 | -0.006 | 0.043 | 0.093 | 0.789 |
| Benzo[b]thiophene | -0.005 | -0.050 | -0.032 | -0.021 | 0.023 | -0.122 | -0.123 | 0.014 | -0.097 | -0.074 | 0.079 | -0.003 | -0.017 | 0.028 | -0.006 | 0.035 |
| 3-methyl-methyl ester Benzoic acid | -0.006 | -0.013 | 0.997 | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| (1-Methylenebut-2enyl)benzene | -0.006 | -0.013 | 0.997 | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| Quinoline | 0.133 | -0.084 | -0.091 | 0.160 | 0.016 | 0.872 | -0.026 | 0.082 | -0.182 | -0.048 | 0.006 | -0.014 | 0.050 | 0.043 | -0.126 | -0.042 |
| 1,3-Benzenedicarbonitrile | -0.040 | 0.779 | -0.026 | -0.031 | 0.090 | -0.079 | 0.044 | 0.001 | 0.029 | -0.011 | 0.018 | 0.346 | 0.457 | 0.131 | -0.020 | 0.009 |
| cis-Stilbene | 0.889 | -0.154 | -0.107 | -0.112 | 0.122 | -0.033 | 0.026 | 0.092 | -0.100 | -0.077 | 0.047 | -0.058 | -0.038 | -0.066 | 0.077 | 0.026 |
| (Z)-7-Hexadecene | -0.006 | -0.013 | 0.997 | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| Benzophenone | -0.012 | 0.882 | -0.025 | -0.018 | 0.040 | -0.059 | 0.026 | 0.010 | 0.023 | 0.037 | 0.004 | 0.422 | -0.057 | 0.015 | -0.015 | 0.006 |
| Benzo[h]quinoline | 0.017 | 0.966 | -0.018 | -0.026 | 0.027 | -0.065 | 0.010 | 0.005 | 0.015 | 0.092 | 0.007 | -0.008 | -0.084 | 0.029 | -0.025 | -0.003 |

Table 3 *(continue)*

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenanthridine | -0.047 | **0.955** | -0.029 | 0.012 | 0.072 | 0.026 | 0.033 | -0.020 | 0.061 | -0.021 | 0.004 | 0.179 | 0.159 | -0.005 | 0.010 | 0.021 |
| (E)-Stilbene | **0.796** | -0.274 | 0.019 | -0.199 | 0.139 | -0.116 | 0.062 | 0.124 | -0.094 | 0.133 | 0.096 | -0.063 | -0.167 | -0.058 | 0.085 | -0.169 |
| o-Terphenyl | **0.903** | 0.090 | 0.141 | -0.038 | -0.072 | 0.026 | 0.020 | -0.266 | -0.036 | -0.013 | 0.026 | -0.069 | -0.003 | 0.071 | 0.072 | -0.065 |
| methyl ester hexadecanoic acid | -0.006 | -0.013 | **0.997** | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| n-hexadecanoic acid | -0.006 | -0.013 | **0.997** | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| Triphenylmethane | -0.052 | 0.334 | -0.024 | 0.003 | 0.042 | -0.020 | 0.039 | 0.012 | 0.024 | -0.067 | -0.002 | **0.899** | 0.013 | -0.014 | 0.008 | 0.018 |
| di-p-Tolylacetylene | -0.011 | -0.013 | -0.011 | **0.853** | 0.033 | -0.143 | -0.020 | 0.063 | 0.037 | -0.064 | -0.187 | -0.026 | -0.103 | 0.224 | 0.040 | -0.051 |
| methyl ester octadecanoic acid | -0.006 | -0.013 | **0.997** | -0.006 | 0.017 | -0.011 | 0.028 | -0.003 | 0.001 | -0.004 | 0.003 | -0.001 | -0.002 | 0.013 | -0.006 | -0.004 |
| m-Terphenyl | **0.878** | -0.086 | -0.055 | -0.020 | -0.216 | 0.151 | -0.006 | -0.146 | -0.036 | -0.049 | 0.061 | 0.014 | 0.026 | 0.038 | -0.099 | -0.047 |
| Benzo[kl]xanthene | -0.067 | -0.059 | -0.023 | **0.956** | 0.057 | 0.000 | -0.022 | 0.010 | -0.010 | 0.097 | -0.003 | 0.005 | 0.050 | 0.001 | -0.032 | 0.001 |
| Benzo[c]phenanthrene | **0.862** | -0.085 | -0.059 | -0.018 | -0.055 | 0.040 | 0.111 | -0.057 | 0.144 | -0.102 | -0.160 | 0.001 | 0.012 | -0.151 | -0.055 | 0.216 |
| Benz[a]anthracene | **0.856** | 0.253 | -0.061 | -0.044 | 0.018 | 0.122 | 0.105 | -0.016 | -0.161 | -0.026 | -0.140 | -0.110 | -0.036 | -0.070 | -0.060 | 0.194 |
| Triphenylene | **0.776** | 0.140 | -0.069 | 0.292 | -0.173 | 0.038 | 0.072 | -0.145 | 0.157 | -0.010 | 0.143 | -0.079 | 0.268 | 0.069 | -0.094 | -0.056 |
| Eigenvalue | 11.92 | 7.53 | 6.82 | 4.98 | 3.93 | 3.43 | 2.53 | 2.43 | 2.22 | 1.91 | 1.74 | 1.56 | 1.48 | 1.37 | 1.16 | 1.12 |
| % Total variance | 18.33 | 11.58 | 10.48 | 7.66 | 6.05 | 5.27 | 3.89 | 3.74 | 3.42 | 2.93 | 2.67 | 2.40 | 2.28 | 2.10 | 1.78 | 1.72 |
| Cumulative % variance | 18.33 | 29.91 | 40.40 | 48.06 | 54.11 | 59.38 | 63.27 | 67.01 | 70.43 | 73.36 | 76.04 | 78.44 | 80.71 | 82.82 | 84.60 | 86.33 |

*Note*: Strong loading (>0.75) are shown in bold.

Table 4

*Classification matrix for discriminant analysis of the car paint primer*

| Types of primer | % correct | Types of primer assigned by DA | |
|---|---|---|---|
| | | 1k primer | 2k primer |
| Standard mode DA | | | |
| 1k primer | 100 | 5 | 0 |
| 2k primer | 100 | 0 | 45 |
| Total | 100 | 5 | 45 |
| Forward mode DA | | | |
| 1k primer | 100 | 5 | 0 |
| 2k primer | 100 | 0 | 45 |
| Total | 100 | 5 | 45 |
| Backward mode DA | | | |
| 1k primer | 100 | 5 | 0 |
| 2k primer | 100 | 0 | 45 |
| Total | 100 | 5 | 45 |

Table 5

*Classification functions for discriminant analysis of car primer samples*

| Compounds | Standard mode | | Forward stepwise mode | | Backward stepwise mode | |
|---|---|---|---|---|---|---|
| | 1k | 2k | 1k | 2k | 1k | 2k |
| Benzene | -1441447.618 | -16795.507 | | | -638559.461 | 2814.644 |
| Pyridine | -40944687.829 | -474203.056 | | | -17561028.515 | 96931.418 |
| Toluene | 1995270.795 | 23494.723 | | | 849695.910 | -4485.385 |
| Picolinyl 7,13,16-docosatrienoate | -2831065.997 | -32019.700 | | | -1239189.704 | 6861.102 |
| Ethylbenzene | -7350966.436 | -85136.028 | | | -3128795.210 | 17988.445 |
| o-Xylene | 259065.704 | 2828.988 | | | 118412.628 | -606.394 |
| Phenylacetylene | -4256027.814 | -50816.304 | | | -1781073.452 | 9633.249 |
| Styrene | 700536.209 | 8241.749 | | | 299024.941 | -1564.968 |
| Benzenemethanimine | 6848166.983 | 72835.565 | | | 3110111.278 | -18464.623 |
| Benzaldehyde | -5290716.603 | -52239.454 | | | -2518795.096 | 15463.376 |
| . alpha. -Methylstyrene | -12066779.675 | -130571.615 | | | -5383066.123 | 32674.829 |
| Benzonitrile | 4880848.495 | 54905.953 | | | 2125812.068 | -12384.468 |
| Indene | 2737615.042 | 30625.433 | | | 1197173.072 | -6999.111 |
| Acetophenone | -12126060.982 | -125789.985 | | | -5621381.786 | 33083.632 |
| Cinnamaldehyde, (E)- | 14848496.715 | 149036.072 | | | 7056352.958 | -41283.239 |
| Indolizine | 110940160.620 | 1340844.749 | 441.341 | 284.523 | 46245746.413 | -239284.765 |
| Benzyl nitrile | 3996569.350 | 37083.529 | | | 1940472.641 | -13135.630 |
| 2-Methylindene | 1594699.703 | 16701.774 | | | 724081.629 | -4562.647 |
| Naphthalene | 1331520.775 | 16654.586 | | | 515835.345 | -3268.133 |
| Azulene | -3658782.020 | -37985.575 | | | -1679536.189 | 10356.539 |
| 1-Naphthalenol | 11266848.097 | 126993.690 | | | 4948654.039 | -27325.119 |
| Quinoline | -10286412.580 | -114007.066 | | | -4499208.348 | 27342.574 |
| Isoquinoline | 104436143.696 | 1159032.151 | | | 46083094.564 | -266212.614 |

Table 5 *(continue)*

| | | | | | | |
|---|---|---|---|---|---|---|
| 1,3-Benzenedicarbonitrile | 87446451.883 | 1006893.258 | 99.335 | 60.131 | 37662011.636 | -209067.414 |
| Benzocycloheptatriene | 2908559.426 | 34845.358 | | | 1179039.548 | -7397.322 |
| 9-Octadecene, (E)- | -17983104.984 | -196454.874 | | | -7973240.130 | 48031.193 |
| Dibenzofuran | 5655282.252 | 60878.509 | | | 2532065.913 | -15404.527 |
| cis-Stilbene | -225308.395 | -5503.048 | | | | |
| 1(2H)-Acenaphthylene | -12029492.475 | -127183.904 | | | -5446228.210 | 33609.115 |
| N-Allylphthalimide | 11913340.486 | 133731.283 | | | 5199927.219 | -30240.562 |
| 1H-Phenalene | 923210.568 | 11302.127 | | | 347335.343 | -2763.345 |
| 4-Ethylbiphenyl | -53908726.413 | -605649.768 | | | -23539106.730 | 136113.381 |
| Fluorene | 3765631.345 | 45194.574 | | | 1557260.192 | -8743.814 |
| Benzo[h]quinoline | -13123181.704 | -147194.181 | | | -5839733.116 | 30700.499 |
| Phenanthridine | -107741265.688 | -1192105.329 | | | -47520773.899 | 278750.813 |
| (E)-Stilbene | 7767507.177 | 89122.005 | | | 3343616.094 | -18929.377 |
| 9H-Fluoren-9-one | 30417273.818 | 347322.102 | | | 13212983.897 | -72884.288 |
| Dibenzo [a, e] cyclooctene | -3847294.601 | -47488.353 | | | -1555260.302 | 8493.467 |
| o-Terphenyl | -10109697.258 | -113132.272 | | | -4511505.644 | 23600.828 |
| Triphenylmethane | -40181193.566 | -536631.141 | | | -15236399.172 | 72633.296 |
| Fluoranthene | -3875215.347 | -40697.564 | | | -1745779.751 | 11312.862 |
| Pyrene | -7768013.508 | -88552.562 | | | -3367986.622 | 18915.949 |
| p-Terphenyl | -8176666.898 | -96228.533 | | | -3478688.136 | 18517.307 |
| m-Terphenyl | 7489445.660 | 77952.664 | | | 3558965.610 | -18047.395 |
| Benzo[kl]xanthene | 14486943.084 | 172203.863 | 95.114 | 58.841 | 6243654.465 | -29134.441 |
| Benzo[c]phenanthrene | -142186320.695 | -1624557.001 | | | -61124138.845 | 355347.255 |
| Benz[a]anthracene | 133750853.794 | 1525758.365 | | | 57546046.819 | -335506.879 |
| Triphenylene | -5714616.456 | -58616.908 | | | -2730587.801 | 14266.536 |

## CONCLUSION

The pyrogram of car paint samples showed that Py-GC-MS is a reliable, very informative analytical technique in the analysis of automotive paint in forensic investigation. Since the pyrograms obtained were quite similar, some minor compounds may be considered in differentiating the samples. As the Py-GC-MS datasets were complex, chemometric techniques were applied to the dataset for uncovering the relationship between variables. The strong loadings from PCA revealed the significant compounds in the car paint primer samples. These compounds may be important in the manufacturing of car paint primer. Using forward stepwise mode of DA, the car paint primer samples can be categorised into two types, 1k and 2k based on three compounds, indolizine, 1,3-benzenedicarbonitrile and p-terphenyl.

## ACKNOWLEDGEMENT

## REFERENCES

Borba, F. D. S. L., Honorato, R. S., & de Juan, A. (2015). Use of Raman spectroscopy and chemometrics to distinguish blue ballpoint pen inks. *Forensic Science iInternational, 249*, 73-82.

Burns, D. T., & Doolan, K. P. (2005). A comparison of pyrolysis-gas chromatography-mass spectrometry and Fourier transform infrared spectroscopy for the analysis of a series of modified alkyd paint resins. *ChimicaActa, 539*, 157-164.

Gál, L., Oravec, M., Gemeiner, P., & Čeppan, M. (2015). Principal component analysis for the forensic discrimination of black inkjet inks based on the Vis–NIR fibre optics reflection spectra. *Forensic Science International, 257*, 285-292.

Kim, J. O., & Mueller, C. W. (1987). *Introduction to factor analysis: What it is and how to do it.* Sage University Press, Newbury Park.

Liu, C. W., Lin, K. H., & Kuo, Y. M. (2003). Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Science of the Total Environment, 313*, 77–89.

Milczarek, J. M., Zięba-Palus, J., & Kościelniak, P. (2005). Application of pyrolysis-gas chromatography-mass spectrometry to car paint analysis for forensic purposes. *Problems of Forensic Sciences,* LXI, 7-18.

Muehlethaler, C., Massonnet, G., & Esseiva, P. (2011). The application of chemometrics on Infrared and Raman spectra as a tool for the forensic analysis of paints. *Forensic Science International, 209*, 173-182.

Muehlethaler, C., Massonnet, G., & Esseiva, P. (2014). Discrimination and classification of FTIR spectra of red, blue and green spray paints using a multivariate statistical approach. *Forensic Science International, 244*, 170-178.

Plage B., Berg, A. D., & Luhn, S. (2008). The discrimination of automotive clear coats by pyrolysis-gas chromatography/mass spectrometry and comparison of samples by a chromatogram library software. *Forensic Science International, 177*, 146-152.

Singh, K. P., Malik, A., Mohan, D., Sinha, S., & Singh, V. K. (2004). Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India) - A case study. *Water Research, 38*(18), 3980–3992.

Singh, K. P., Malik, A., Mohan, D., Sinha, S., & Singh, V. K. (2005). Chemometric data analysis of pollutant in wastewater case study. *Analytical ChimicaActa, 532*, 15–25.

Trzcińska, B., Zięba-Palus, J., & Kościelniak, P. (2009). Application of microspectrometry in the visible range to differentiation of car paints for forensic purposes. *Journal of Molecular Structure, 924–926*, 393-399.

Vega, M., Pardo, R., Barrado, E., & Deban, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research, 32*, 3581–3592.

Zięba-Palus, J., Michalska, A., & Wesełucha-Birczyn ́, A. (2011). Characterisation of paint samples by infrared and Raman spectroscopy for criminalistic purposes. *Journal of Molecular Structure, 993*, 134-141.

Zięba-Palus, J., Zadora, G., & Milczarek, J. M. (2008). Differentiation and evaluation of evidence value of styrene acrylic urethane topcoat car paints analysed by pyrolysis-gas chromatography. *Journal of Chromatography A, 1179*, 47-58.

Zięba-Palus, J., Zadora, G., Milczarek, J. M., & Kościelniak, P. (2008). Pyrolysis-gas chromatography/ mass spectrometry analysis as a useful tool in forensic examination of automotive paint traces. *Journal of Chromatography A, 1179*, 41-46.