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GAS CHROMATOGRAPHY ANALYSIS OF RESIDUAL GASOLINE ON FLOORING MATERIAL IN RELATION TO DURATION OF SAMPLING

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ABSTRACT: Determination and confirmation of the presence of residual gasoline in a fire scene is important to prove arson. In most fire cases, substrates carrying absorption behaviour, such as carpet, were preferable for evidential sampling. However, non-porous substrates shall also not be overlooked by the fire investigators where such evidence could potentially contain residual gasoline to be analysed. This study was aimed to detect the presence of residual gasoline on non-porous flooring material and evaluate its persistence in relation to the duration of sampling. In this study, unburnt and burned mosaic tiles were allowed for evaporation at different time interval up to five days (60 hours) duration separately, followed by gas chromatography (GC) analysis. Based on the GC chromatogram, its severe vaporisation was evident during the first hour for both settings followed by continuous but non-linear decrease with time elapsed. Data points in a score plot generated upon principal component analysis (PCA) demonstrated the variations among the gasoline profiles. For the burnt sample, by evaluating the GC profiles and the outcome of PCA with the percentage of gasoline peak lost along with time elapsed, it was concluded that the maximum survival time for burnt gasoline on the flooring mosaic tile could still be detected up to five days. On the contrary, the survival of gasoline for unburnt tiles could be only up to 48 hours. Therefore, appropriate sampling and preservation strategies shall be established to assist the determination of the existence of arson activity through the detection of residual gasoline.

Keywords: Forensic science, fire investigation, gasoline, floorings, gas chromatography, time elapsed.

INTRODUCTION

Arson is a generic term used for the setting of a deliberate and malicious fire to damage the property of another person [1]. Usually, it requires the detection of related forensic evidence to confirm an arson, and to determine if a fire is a deliberated or intentional act [2]. During the investigation, determining the presence of accelerant is of forensic importance. In the context of a suspicious fire, an accelerant is the substance, more specifically a typical ignitable liquid, that has been deliberately introduced to the scene to facilitate the spread of fire [3]. Among the accelerants, gasoline which famed as petrol is commonly used by arsonists to cause fires as it is readily obtainable and cheap [4].

Securing important forensic evidence related to a fire case could be difficult due to the destructive nature of fire. In many instances, the available forensic evidence could have been destroyed, including the volatile ignitable liquid to link any source or suspect to the fire scene [5]. Furthermore, such ignitable liquids also tend to change from their original form as they could undergo evaporation and pyrolysis processes [6]. In fact, highly volatile components in ignitable liquid may be lost readily as compared to low volatility components [5,6].

Studies on the analysis of ignitable liquid and its related compounds have been published in literature and have undoubtedly provided significant contributions to the advancement of forensic analysis. However, it is worth noting that majority of the published studies were focused on profiling of ignitable liquid as well as the advancement of analytical technique towards more sensitive detection. On the substrate-based detection, studies were more focused on the detection of gasoline residue in the burnt or unburnt porous surfaces, including wood, cloth, carpet, chipboard, and shoe [7-9];

however, less likely to discover the presence of residual ignitable liquid on non-porous surfaces such as flooring materials. In view of this, this study focused on the analysis of residual gasoline on non-porous mosaic tiles and determination of the appropriate duration of sampling for maximum recoverability of gasoline after a fire. Note that mosaic tile was used in this study as it is commonly used in Malaysian's structure to cover and protect the floor. Moreover, the possibility of finding gasoline on the floor is relatively higher, if such ignitable liquid was used in an arson act, either burnt or unburned. It is hoped that this study would suggest the suitable evidence sampling and preservation strategies for the detection of residual gasoline on the mosaic tile surfaces, which frequently overlooked by the forensic investigators, and subsequently determine the existence of arson activity.

MATERIALS AND METHODS

Materials and chemicals

Gasoline (RON 95, Petronas®, Malaysia) was obtained from a petrol service station near the research laboratory. Plain mosaic flooring tiles that were commonly available in residential structures were obtained commercially from a hardware store. Analytical grade acetone and GC grade *n*-hexane were purchased from Merck (Kenilworth, NJ).

Preparation of mosaic tiles

All the mosaic tiles (8 inch × 8 inch) were cleaned with acetone to remove dust or contaminant from the surface. Then, each tile was poured with 20 mL of gasoline in a spiral movement from the middle to the circumstance to ensure the whole piece of tile was covered with gasoline.

In this study, two experimental settings were investigated. To study the persistence of gasoline on a surface, mosaic tiles poured with gasoline were left in ambient temperature (≈25°C) for the set duration prior to sampling and analysis. On the other hand, mosaic tiles with gasoline were ignited and burned until self-extinguished, and subsequently subjected to exposure at the same environment for the same duration as in the previous experiment. In triplicate, both the unburnt and burned mosaic tiles could evaporate at different time interval up to five days (60 hours) duration separately, making a total of 90 samples. Fresh gasoline prepared in a dilution of 1:20 v/v using *n*-hexane was used to generate the reference GC chromatogram. Unburnt mosaic tiles with gasoline served as positive control whereas tiles without gasoline acted as negative control.

Sample extraction

A piece of filter paper (Sartorius AG, Göttingen, Germany) was cut into half. The filter paper was pre-wetted with *n*-hexane and used to wipe any residual gasoline from the surface of mosaic tiles covering 64 inch^2. The wiping was initiated in an outer corner and ended in the centre of the tile following a concentric pattern. With the wiped area facing in, the filter paper was folded, and the surface of the mosaic tile was again wiped from the opposite direction. After the procedure, the wiped area was folded in and inserted into a 20 mL glass vial (Supelco, Bellefonte, PA). Solvent extraction was carried out by adding 10 mL of *n*-hexane into each sample vial with the filter paper and allowing it to stand for one hour. It is important to ensure the filter paper was completely submerged into the solution contained in the capped and labelled glass vial. After an hour, all samples were filtered using 0.45 µm syringe filter (Merck Millipore, MA) and transferred to the vials for GC analysis.

GC-FID analysis

GC-FID analysis was carried out using 7890A gas chromatography-flame ionisation detector (GC-FID) equipped with G4513A series autosampler (Agilent Technologies, Santa Clara, CA) with a HP-5 capillary column (30 m × 0.32 mm × 0.25 µm film thickness) purchased from Agilent Technologies (Santa Clara, CA). With a flow rate of 1.2 mL/min, purified nitrogen gas (99.9%) was used as the carrier gas. A split mode (10:1) was conducted and the injector temperature was set at 300 °C. Chromatography separation was achieved using 50 °C as initial temperature and held for 2.5 mins, followed by an increase of 15 °C/min to 250 °C and held for 5.83 mins. The detector temperature was set at 300 °C. Hydrogen flow, air flow and make up gas flow was set at 30, 300 and 15 mL/min, respectively. GC automation and data analysis were performed using Chemstation software (Rev. B.04.02, Agilent Technologies, Santa Clara, CA). All extracted samples including positive and negative controls were analysed. Blank was run between each sample to avoid carry-over. All gas chromatograms were compared and evaluated.

Data analysis

Peaks areas from the selected peaks were integrated and transferred to Microsoft Excel® (Redmond, WA). Multivariate principal component analysis (PCA) was performed using Minitab 18 software (Minitab Inc., State College, PA) after performing normalisation by dividing the area of selected peaks to the total area of all peaks. The PCA score plot was used to determine the clustering of samples, if any, in relation to the duration of sampling based on their chromatographic profiles.

RESULTS AND DISCUSSION

GC-FID analysis

The analytical parameters used in this study were adapted from ASTM E1618-06 method [10]. Representative chromatograms for neat gasoline (1:20 v/v), positive and negative controls were demonstrated in Figure 1. Based on the chromatograms, profile of neat gasoline [Figure 1(a)] was found very similar to the profile of positive control [Figure 1(b)], indicating the sample extraction procedure using filter paper did not contribute to additional interfering peaks which could potentially influence the GC interpretation. The diagnostic gasoline profile was identified by the presence of five peaks C3- alkylbenzene and C4- alkylbenzene which consisted of a series of peak doublets [11]. In the chromatogram of negative control, no observable interference was detected [Figure 1(c)]. Note that the same gasoline sample was used throughout this study to avoid the variation in chromatographic profiles as different gasoline samples could affect have slightly different profiles and affected the experimental results. In fact, for the comparison on the influence of burning as well as the duration of sampling towards the chromatographic profiles, the identification of individual compounds was not a crucial criterion, but this study involved the relative comparison among peaks of similar retention times and their respective peak areas.

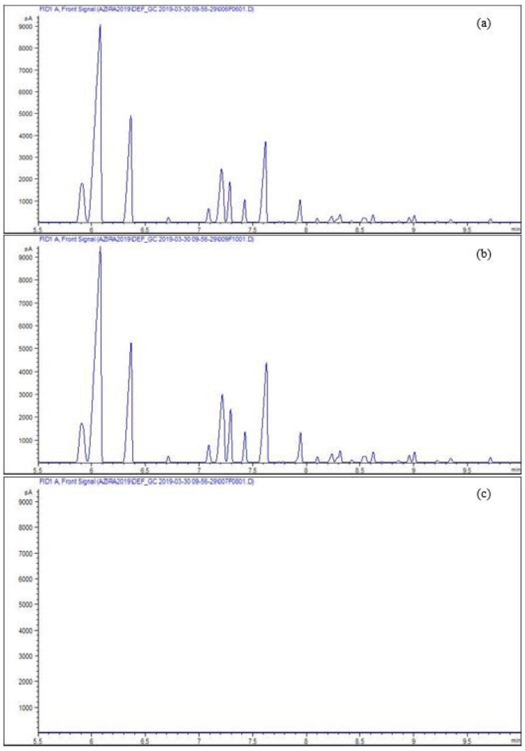

Figure 1. Representative chromatogram of (a) neat gasoline, (b) positive control, and (c) negative control.

Due to complex nature of gasoline profiles, well-separated and symmetrical peaks were selected for interpretation. In this study, a total of 39 peaks lied between 6 minutes and 16 minutes were selected and distributed into 11 different regions (*i.e.* regions A to K) for statistical analysis.

Investigation of gasoline profile with time elapsed on the surface of non-porous mosaic tile

Figure 2 demonstrates the relationship between percentage of peak areas in the respective regions against the time elapsed upon the application of gasoline on the surface. A declining trend of peaks area was observed from Region A to I with extended environmental exposure with the exception of region J and K. Such observation indicated that the individual compounds in the regions where the peaks were eluted earlier tend to decrease with prolonged time due to evaporation. In fact, the peaks with shorter retention times could have possessed lower boiling points as compared to those with higher retention times. Lighter and more volatile compounds were rapidly evaporated than heavier components. Therefore, these peaks could have evaporated from the surface of the mosaic tiles upon exposure, and gradually the chromatographic profiles of the samples subjected to longer exposure would be dominated by the greater retained peaks. Therefore, when ignitable liquids were subjected to evaporation or environmental exposure, the composition could be altered and tends to lose the more volatile or lighter components.

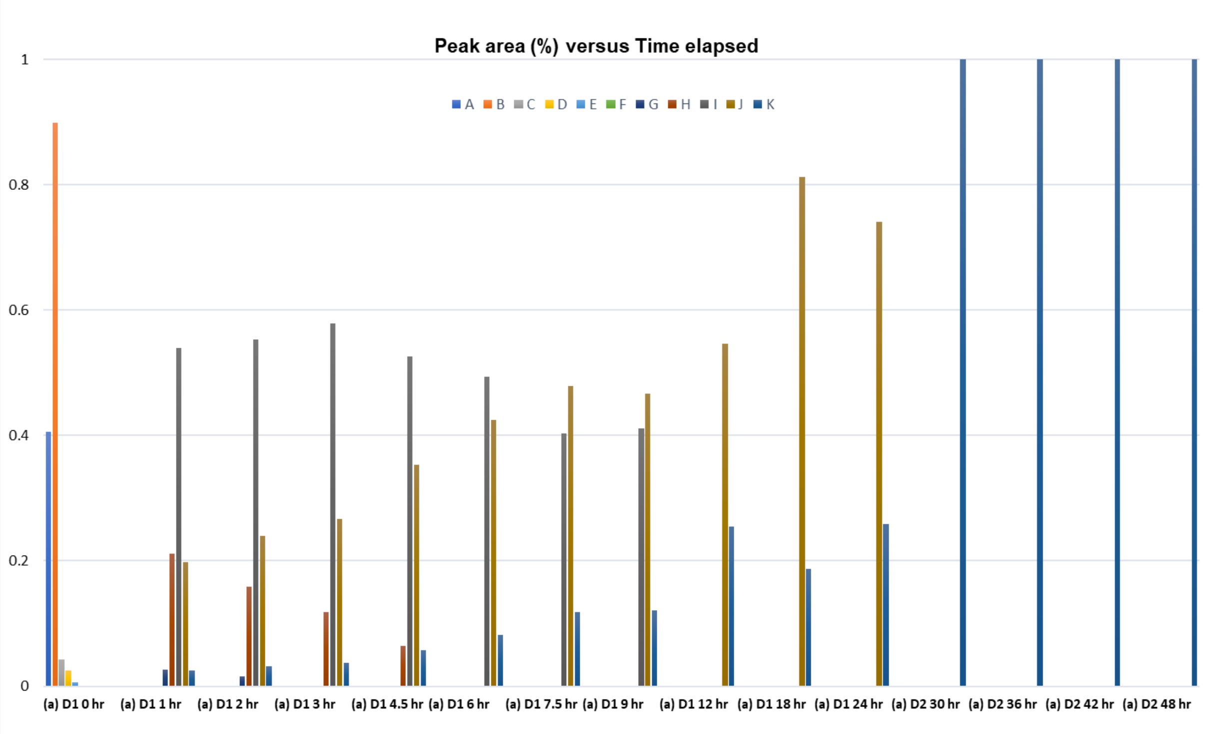

Figure 2. Bar chart of percentage of peak area versus time elapsed after fire for unburnt tiles setting.

Figure 3 demonstrates the percentages of peaks area in each region against time elapsed after fire for burnt samples. Peaks eluted between the Regions A to F, characterised by peaks of lower retention time were only observable in the chromatogram of one hour elapsed after the burning. A drastic loss of light volatile compounds was evident as compared to heavy non-volatile compounds. Peaks in the Regions H and I could behave slightly volatile was still observable upon 48 hours and 12 hours exposure, respectively. Peaks in the higher retention time regions, namely Regions J and K remained and shown in the respective chromatogram up to five days duration.

Upon burning and subjected to environmental exposure, a non-linear decreasing trend was discovered. This study clearly showed that it was possible to recover residual gasoline from burnt tiles up to 120 hours. This could propose that residual gasoline could be mainly consisted of components behaving slightly and high volatile compounds were protected from vaporisation by the upper concealment layer of soot following a fire.

Principal component analysis

Based on the visual comparison of chromatographic profiles and the relative comparison of the peak areas, it could suggest the time duration since the application of gasoline on the mosaic tile surfaces as well as the time elapsed since the burning. Subsequently, multivariate analysis was performed to determine the trend of profile change in the sample subjected to environmental exposure both without and with burnings. Most variations were spotted in the region where compounds of slightly volatile and non-volatile located (Region G to K) upon different time exposure in unburnt and burnt tiles setting. Selected peaks from these regions were subjected to PCA analysis following normalisation. Figure 4 depicts the score plot for unburnt tiles with 73.6% explained variance while score plot of burnt tiles setting accounted for 63.3% variance was demonstrated in Figure 5.

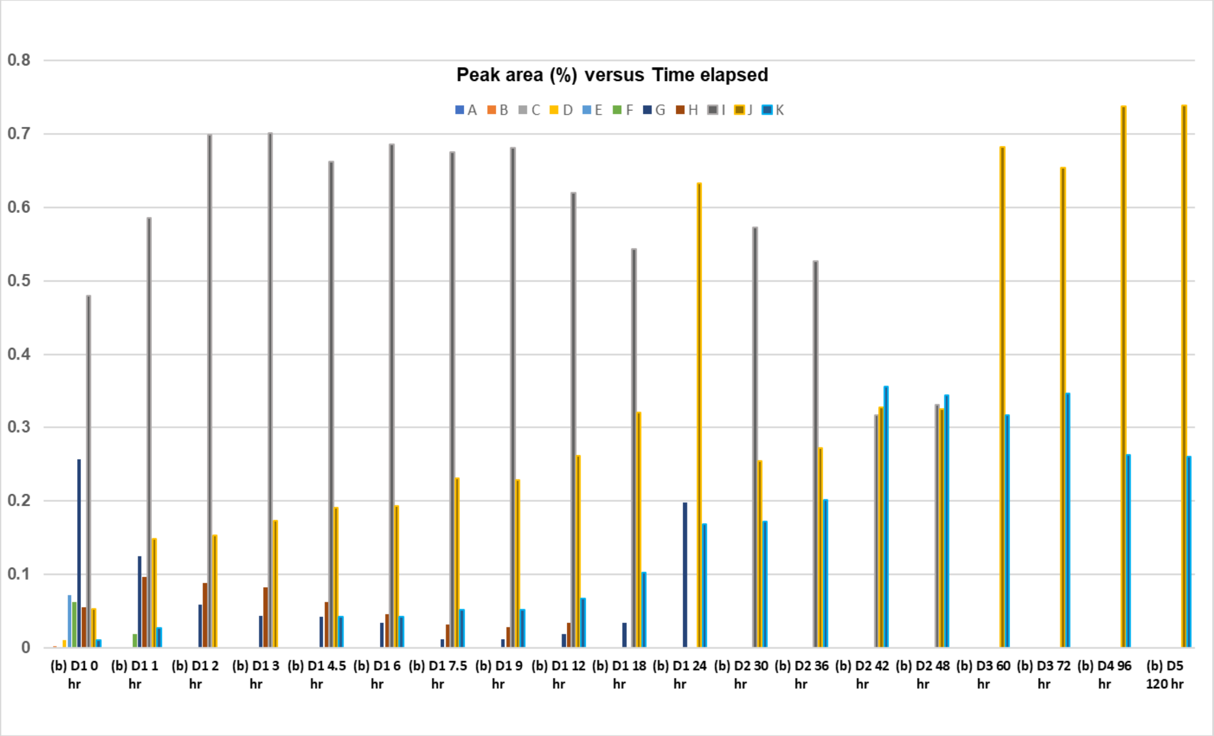

Figure 3. Bar chart of percentage of peak area versus time elapsed after fire for burnt tiles setting.

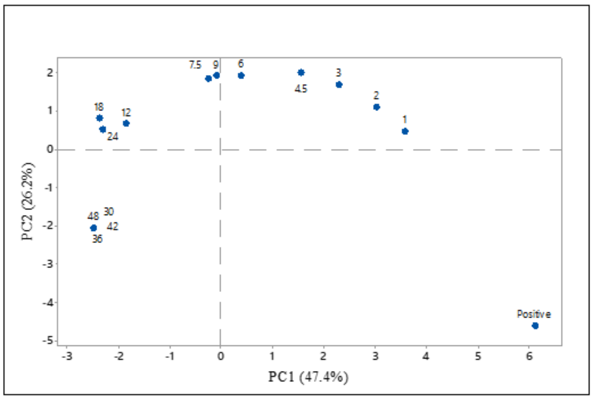

Figure 4. PCA score plot for unburnt tiles setting (Each number representing the time elapsed in hour).

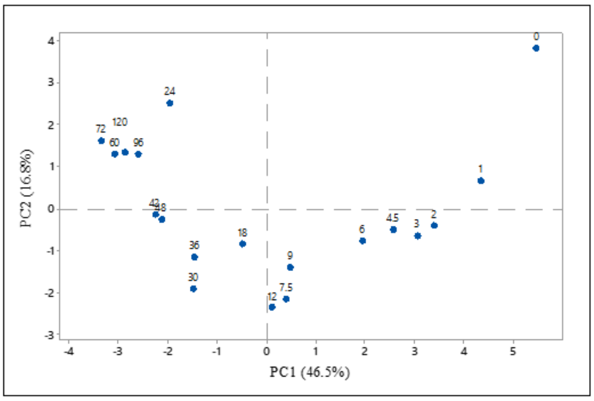

Figure 5. PCA score plot for burnt tiles setting (Each number representing the time elapsed in hour).

Generally, the data points seem to distribute from right to left as the time elapsed for the sampling increase for the unburnt tiles setting (Figure 4). The data points representing sample collected at first hour until 24 hours were located on the first and second quadrant of PCA plot forming a positive score for PC1 (47.4%). Grouping was observed for gasoline collected from 6 hours to 9 hours and 12 hours to 24 hours. Gasoline acquired upon 1 hour to 4.5 hours illustrated a similar profile but separable with reference to PC1. Those gasoline collected from 30 hours to 48 hours were clustered together at quadrant III of the score plot, separated away from others based on the PC2 (26.2%). Positive control for unburnt tiles in this study reflected its uniqueness by locating at the fourth quadrant of the score plot.

Similar to unburnt tiles setting, the data acquired from burnt tiles setting shifted from right to left as time elapsed for sampling increase (Figure 5). Gasoline sampled from first hour to 12 hours were found in second and third quadrant of score plot, associated with positive score plot of PC1 (46.5%). Those gasoline collected upon first hour to 6 hours tended to exhibit a similar profile; however, distinguishable based on the PC1. Sample collected at time 7.5 hour to 12 hours appeared to cluster together and distributed away from gasoline collected from first hour to 6 hours based on PC2 (16.8%). Variation among the gasoline profile sampled from 18 hours to 36 hours could be explained *via* PC1 and PC2 of score plot. Gasoline collected at 24 hours located near to grouping of those collected from 60 hours to 120 hours. Meanwhile, clustering was observed for the gasoline sampled from 42 hours and 48 hours as well as 60 hours to 120 hours. Sample collected upon zero hour was located at the corner of the second quadrant demonstrated its remarkable differences with other samples collected at different duration.

CONCLUSION

Overall, unburnt and burnt gasoline samples recovered from mosaic tiles using GC technique were studied and investigated. The effect of duration of sampling towards the detection of gasoline residue on flooring mosaic tile was high. It was found that with prolonged duration of sampling, the number of peaks lost increases due to evaporation process, especially for gasoline compounds with low boiling points that appeared at lower retention time. From the experimental result, it was found that the survival of gasoline for unburnt tiles could be up to 48 hours, whereas for burnt tiles, gasoline residue could still be detected up to 120 hours. Therefore, appropriate evidence sampling and preservation strategy for the detection of residual gasoline on the mosaic tile surfaces shall be established to assist the determination of the existence of arson activity.

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