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Gas Chromatography Based Forensic Analysis of Gasoline from Burnt Carpets Retrieved Using Different Fire Extinguishing Methods

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ABSTRACT: The detection of ignitable liquid residues is important in confirming the possibility arson in fire scene investigations. However, destruction due to fire and subsequent fire extinguishing activities challenge the detection of ignitable liquid residues after a fire. In view of this, we aimed to investigate the potential influence of different fire extinguishing methods against the detection of gasoline residues on carpets subjected to fire under controlled conditions. In this study, carpets doused with gasoline were burnt and the fire was extinguished following five methods all simulating regular operational procedures viz. the use of ABC powder fire extinguisher, water, fire retardant fabric, sand and, lastly, letting the fire to perish due to self-extinguishment. Profiles of gasoline residue from different simulated conditions were generated through gas chromatography and were then analysed by chemometric method. Our experimental results revealed no observable interfering products that could be attributed to the different extinguishing methods. The profiles of gasoline were similar to the profile of neat gasoline, with certain degree of chromatographic shift possibly due to loss of lighter hydrocarbon compounds. Subsequently, principal component analysis is seen to offer a more objective characterisation, allowing the discrimination of samples subjected to water extinguishing method from the others. In conclusion, the use of varying fire extinguishing methods did not influence the possibility to detect gasoline on burnt carpets under our experimental conditions. Residues of gasoline could still be detected although subjected to extinguishment since gasoline does not appear to be totally burnt during a fire.

Keywords: forensic science, chromatography, incendiary fire, gasoline, extinguishing methods

Introduction

Fire breakouts are not uncommon in Malaysia. In recent year, the highest among such breakouts was 54,540 cases recorded in 2014. Although it the foregoing figure is deemed lesser compared to 40,865 and 43,437 cases respectively during 2015 and 2016 (up to September), still an average of 160 fire outbreaks per day poses a significant threat to our national development due to the destructive nature of fire in causing loss of property and money, or even injuries or death [1-2]. According to statistics released by the Fire Investigation Division, incendiary fire was one of the main contributors accounting for 5271 cases reported in 2015 alone which slightly decreased to 4,442 cases during the period of January to September of 2016 [2]. During the nine month period up to September 2016, 435 arson cases were reported [2]. Although this figure accounted for only 1.1% of the total of 43,437 fire breakout cases, they need to be taken seriously in view of their criminal nature and hence potentiality to threaten public safety.

Forensic fire investigation always involves the determination of the origin of fire as well as the cause of fire such as accidental or incendiary. An act of igniting a fire with deliberate intent is classified as incendiary fire, whereas accidental fire does not involve intentional ignition [3]. In actual case situations, determining the incendiary or accidental nature of fire is often difficult, and an obvious indicator is the presence of residues of ignitable liquids at the fire scene [4-5]. Such presence is considered evidence indicating intention of using liquid accelerants to promote the initiation and spread of fire supporting the hypothesis of an incendiary fire [5].

In most fire cases, the destructive nature of fire tends to destroy the evidence indicating an incendiary fire. In other words, the chance of detecting sufficient liquid accelerant remaining unaltered in a fire scene is relatively low [6], and even when present, fire suppressing and extinguishing methods may further destroy the available ignitable liquid residue contaminate such residues affecting their detection and interpretation during analysis. Hence, this study was designed to simulate incendiary fire involving gasoline and evaluating the extent of detection of residue after applying different extinguishing methods to extinguish the fire. Possible potential interference attributable to various extinguishing methods was investigated. Residues of ignitable liquid, here gasoline, present on the retrieved burnt carpets were analysed using gas chromatography technique followed by chemometric analysis.

Materials and methods

Materials and Chemicals

Gasoline (RON 95, Petronas, Kota Bharu) was obtained from a petrol station near our research laboratory. A common household cotton type carpet was used as substrate. Water, sand, fire retardant fabric and ABC powders were used to extinguish the simulated fire in this study. Note that these materials are commonly used during extinguishing procedure. Analytical grade dichloromethane (DCM) was purchased from Merck (Whitehouse Station, NJ) to dissolve the samples prior to introduction into analytical system.

Preparation of Carpet Samples Subjected to Extinguishments

New household carpets were cut into square of 12 cm × 12 cm. The carpet was placed at the center of square metal cans of 18 cm × 15 cm. Then, 20 mL of gasoline was poured at the middle of the carpet. Fire was initiated using matches and then each gasoline soaked carpet was let to burn for 30 seconds followed by extinguishment of fire. Four different extinguishing methods, namely by water, sand, ABC powder and fire cloth were simulated with three repetitions for each. Additional three samples were subjected to completely burning until ash, making up to 15 samples in total. Unburnt carpet samples with gasoline were used as positive control and carpet samples without gasoline were used as negative control.

After putting offthe fire, three strips of 1 cm × 3 cm from each materials were randomly cut from any region of each burnt carpet sample and placed separately in 20 mL glass vial (Supelco, Bellefonte, PA). Solvent extraction was achieved by adding 15 mL of DCM into the vials with samples and leaving it to stand overnight. All samples were then transferred and filtered into GC vials prior to instrumental analysis.

GC-FID Analysis

Analysis of gasoline from carpet samples subjected to different extinguishing methods was carried out using a 7890A gas chromatography-flame ionisation detector (GC-FID) equipped with 7963 series autosampler (Agilent Technologies, Santa Clara, CA). Chromatography was achieved using a HP-5 capillary column (30 m ×0.25 mm × 0.25 μm film thickness) purchased from Agilent Technologies. Purified nitrogen gas (99.9%) was used as carrier gas with constant flow rate of 1.2 mL/min. Split mode (10:1) injection technique was performed at 300°C as inlet temperature to vapourise the sample. Oven was set at 50°C as initial temperature for 2.5 min, ramp of 15 °C/min to 250 °C, and held for 5.83 min. Detector temperature was set at 300 °C and the total run time was approximately 20 minutes. Hydrogen flow, air flow and purified nitrogen gas were set at 30, 300 and 15 mL/min, respectively. Chemstation software (Rev. B.04.02, Agilent Technologies) was used for GC automation and data analysis.

All extracted samples including positive and negative controls were analysed. Prior to analysis of burnt samples, neat gasoline was diluted with DCM (1:4, v/v) and analysed to obtain its reference chromatogram. Gas chromatogram of each sample was compared and evaluated.

Statistical Analysis

For multivariate analysis, 24 selected peaks from gas chromatograms were normalised using Microsoft Excel® (Redmond, WA). Upon normalisation, these variables were subjected to Principle Component Analysis (PCA) using Minitab 16 software (Minitab Inc., State College, PA).

Results and Discussion

Gasoline Profile

The reference chromatogram obtained through the analysis of neat gasoline, Figure 1 (a), comprised of numerous compounds, forming a complex with resolved and unresolved peaks. According to ASTM E1618 (2014), identification of gasoline involves the determination of alkanes, cycloalkanes, aromatics and condensed ring aromatics patterns [7]. In this study, the respective peaks on the chromatograms were not identified individually, but the focus was on the comparison of the potential matrix effect of extinguishing methods and substrate against gasoline profiles. The use of only one type of gasoline from the same source throughout the study avoided any deviation of the profile due to batch variations and environmental insults such as weathering.

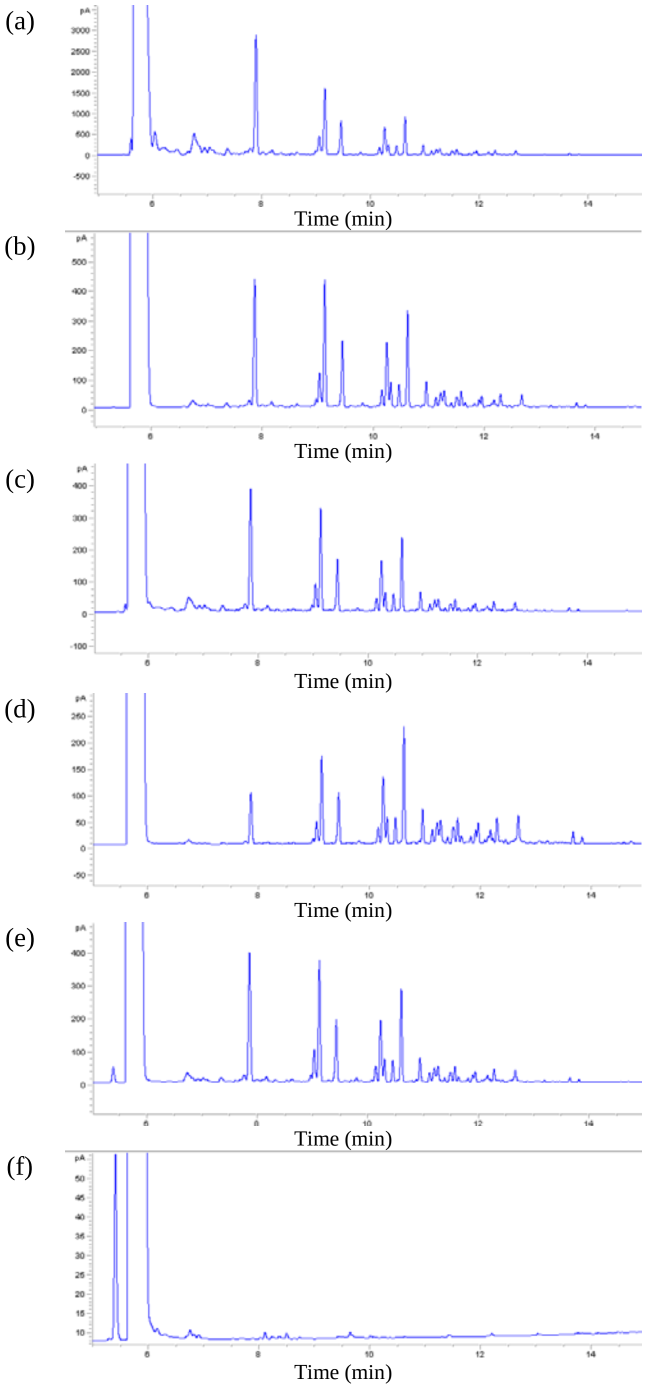

Figure 1: Representative chromatograms of burnt carpet subjected to (a) positive control; (b) ABC powder fire extinguisher; (c) water; (d) fire retardant fabric; (e) sand and (f) complete burning

Chromatograms of burnt carpet samples subjected to five different extinguishing methods are illustrated in Figure 1. At a glance, similar gasoline residue profiles are seen demonstrated by all the samples, except the one in which the carpet was burnt into ashes, Figure 1(f) wherein no significant peaks could be observed. In other words, under the experimental control, residues of gasoline could still be detected in partially burnt carpets by GC although subjected to extinguishments, unless the carpet is totally burnt in to ashes during a fire.

Exploratory Analysis

For the purpose of non-target screening of gasoline profile across the chromatogram, 24 peaks of good resolution and well-defined peak shape were arbitory selected at the retention times as indicated in Table 1. Peak areas of each selected peak were determined followed by normalisation to correct the multiplicative scaling effect, ensuring the data suitability for multivariate statistical analysis. Selected peak, upon proper data treatment, may aid easier pattern recognition and allow simple explanation on the similarity or dissimilarity between samples. In this study, PCA was chosen for classification to visualise the potential grouping of burnt carpet samples on the basis of their extinguishing methods.

Table 1: Selected peaks used for PCA

Peak	Retention Time (min)	Peak	Retention Time (min)
Peak 1	6.93	Peak 13	10.62
Peak 2	7.36	Peak 14	10.95
Peak 3	7.88	Peak 15	11.12
Peak 4	8.34	Peak 16	11.21
Peak 5	9.04	Peak 17	11.28
Peak 6	9.15	Peak 18	11.50
Peak 7	9.44	Peak 19	11.58
Peak 8	9.81	Peak 20	11.65
Peak 9	10.15	Peak 21	11.90
Peak 10	10.24	Peak 22	11.95
Peak 11	10.31	Peak 23	12.29
Peak 12	10.46	Peak 24	12.67

Principle Component Analysis

PCA extracts multivariate data information through statistic and mathematical tools. In this study, PCA was performed to cluster the simulated carpet samples to observe any variation which could have come from different extinguishing methods. The score plot was developed with the first two PCs, which was accounted for 74.8% of explained variance, Figure 2.

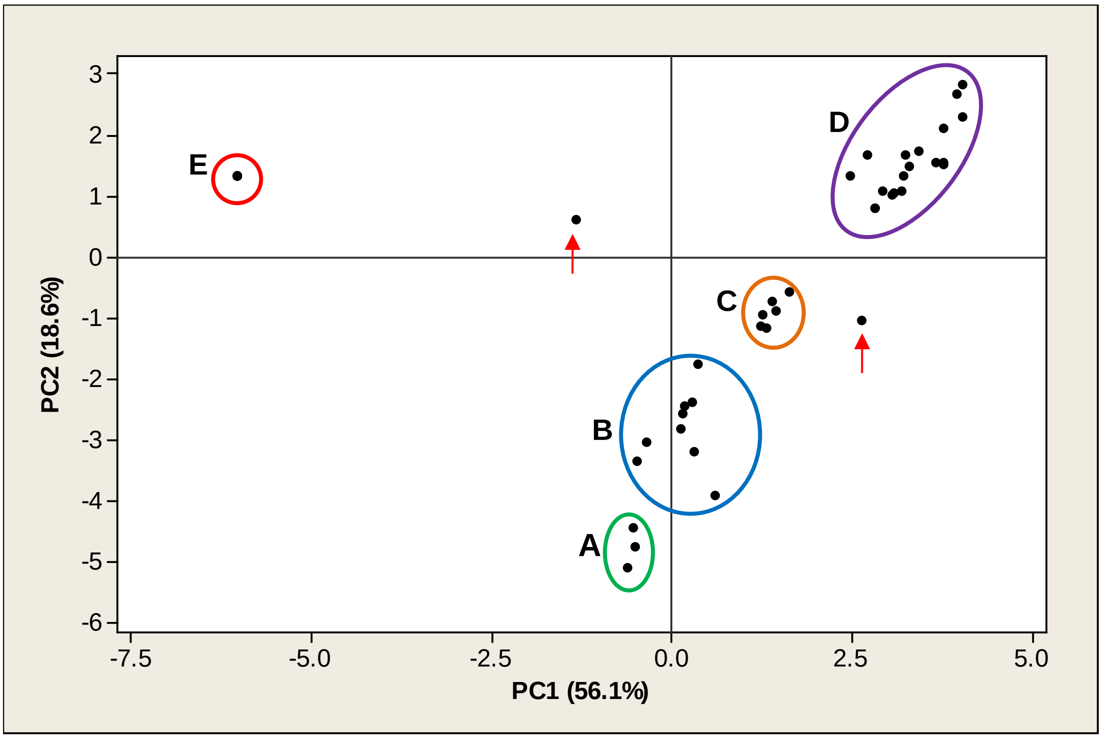

Figure 2: Score plot of gasoline residue samples subjected to different extinguishing methods

From the score plot, five main clusters (Cluster A, B, C, D and E) were evident. PC1 (56.1%) separated negative samples (without the presence of any gasoline) from those presented with gasoline in this study. PC1 allowed discrimination of samples as a function of gasoline content in the simulated carpet samples. Note that carpet samples burnt into ash were grouped together with negative samples (Cluster E), indicating the absence of gasoline due to complete burning. Therefore, in conspicuous fire, fire rescue should be carried out as soon as possible before the completion of burning of gasoline or other possible ignitable liquid which could have been utilised for incendiary purposes. This information is vital as a fire investigator is required to determine a fire cause, either accidental or deliberate act [8].

In contrary to PC1, PC2 (18.6%) could have aided in discriminating our samples on the basis of the concentration of gasoline which is indicated by their respective peak intensity. Samples in Cluster D were justified to be away from positive samples (Cluster A) as a majority of them showed relatively lower peaks. Cluster D consisted of all extinguishing methods considered in this study, except those extinguished by water. Hence, it can be suggested that gasoline is the fuel that sustains to support a fire once ignited until the prevention of oxygen supply by any means, and finally putting out the fire. In this case, ABC powder, cloth and sand prevented the continuos supply of oxygen resulting in extinguishing the fire. Through PCA, these three extinguishing methods could not be differentiated and thus remained indistinguishable from each other.

Two samples extinguished with ABC powder and sand respectively, formed another cluster (Cluster C) separated from the main cluster D. In this study, the same volume of gasoline was applied in every sample, but the burning process could also be affected by the burning rate, ignition site of burning, and other undetermined environmental factors. These factors could lead to either slower or faster burning, which can be indicated by the intensity of gasoline residue after extinguishment. Samples in Cluster C could have retained more gasoline, deviating more towards the Cluster A (positive samples) and away from the expected cluster (Cluster D) in the score plot. Hence, a fire is still an uncontrollable phenomenon which could lead to variation, especially in term of gasoline residue, although the study was carried out in a controlled environment with similar procedure. Even on the same piece of carpet sample subjected to same extinguishing method, chromatograms could vary as indicated by arrow in the score plot, possibly due to variations in the initial concentration of gasoline that spread in the carpet as well as due additional undetermined contaminants in the carpet all of which could have influenced the burning process.

An interesting observation in this study was the formation of Cluster B by the burnt samples extinguished by water. These samples did not fall together in the main cluster with other extinguishing methods, instead, formed a separate cluster located nearer to positive samples. This result showed that these samples indicated relatively higher amount of gasoline residues compared to those recovered in other extinguishing methods. Other methods, namely ABC powder, cloth and sand work by creating a barrier preventing the oxygen to support a fire. Contrarily, applying water to a burning carpet could have lowered the temperature below the ignition temperature, and therefore reducing the pyrolysis rate of gasoline [9]. The cooling effect of water could have minimised the chance of gasoline to further vapourise to the surroundings and thus generating peaks of greater intensities in the chromatograms.

Conclusion

Analysis of ignitable liquid residues is important to confirm an incendiary fire. In this study, the effect of different fire extinguishing methods in influencing the possibility to detect gasoline residues on burnt carpets was investigated. Our analytical results showed that a detectable amount of gasoline residues could still be recovered from burnt carpets although they were subjected to different extinguishing methods. In our hands, the product arising from extinguishing methods did not interfere or restrict the possibility to characterise gasoline residues based. Our findings that residues of gasoline could still be detected although subjected to extinguishment unless the substrate was completely burnt to ashes could benefit fire investigation, especially those involving the recovery of gasoline from a fire scene.

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