Characterisation of Background and Pyrolysis Products that May Interfere with Forensic Analysis of Fire Debris in Mauritius

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Abstract

Petrol is one of the most commonly used liquid accelerants in arson cases. It is identified by the presence of an abundance of aromatic compounds whose peaks cluster in specific patterns. The positive identification of these target compounds suggests the presence of the petrol in the debris. This information can assist a fire investigator in determining the cause of the fire, including whether or not arson is suspected. The current research aims at studying the legitimate background products in fire debris, including their identification and characterisation. A range of substrates commonly encountered at fire scenes in Mauritius were analysed in the presence and absence of petrol using the passive headspace absorption method. In unburnt samples, a number of interfering products were identified and some of the hydrocarbons liberated were those commonly found in petrol. When comparing the results of the burnt with the unburnt samples, it was found that only a small proportion of the volatiles detected in the burnt items were due to pyrolytic products and the rest were attributed to residues originally present in the unburnt items. Samples analysed in the presence of petrol, revealed that the concentration of these interfering products were below the detection limit for the accelerant and thus did not cause misinterpretation of the data.

Keywords: Fire investigation, background interferences, passive headspace concentration, GC-MS
1. Introduction

Many modern synthetic materials found in our environment are of petrochemical origin and when they are exposed to fire conditions, they produce a number of products in the boiling point range of commonly encountered ignitable liquids [1-8]. These interfering products include either petroleum products that are already absorbed onto the surface or they can be products due to pyrolysis or incomplete combustion of substrates [9-12]. Common ignitable liquids, including Isopar H, used in the manufacture of vinyl sheet flooring, toluene in glue or kerosene in the printing industry are often identified in fire debris [1, 10, 13]. Depending upon the type of polymer the substrates are made up of, thermal decomposition could result in the formation of compounds such as toluene, xylene, and other complex volatiles, which are legitimately from the background interference products [14, 15].

Ettling and Adams were the first ones to describe the production of some hydrocarbons through the pyrolysis of wood, fabrics and papers although they did not identify the pyrolysis products [16]. Since then, there have been a number of reports on pyrolysis products and/or background hydrocarbons which can interfere in the identification of petrol [17-21]. The purpose of the present study is to identify and characterise hydrocarbons which although merely forms part of the background environment may interfere with the identification of petrol. Moreover to evaluate the use of sequential ratios of isomeric hydrocarbons to determine the degree of evaporation of petrol samples

2. Materials and methods

2.1 Material

The ignitable liquid used in this study is unleaded petrol obtained from the local gas station of Shell Petroleum Company. n-Pentane (HPLC grade) was purchased from Romil Ltd. Eleven different substrates commonly found in homes or buildings obtained either from the University of Mauritius or from local industries were used. Table 1 lists all the products analysed during the course of this study.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>Cuttings of white cotton cloth use in the manufacture of T-shirts</td>
</tr>
<tr>
<td>2.</td>
<td>Old vinyl floorings</td>
</tr>
<tr>
<td>3.</td>
<td>New vinyl floorings</td>
</tr>
<tr>
<td>4.</td>
<td>Carpet – new</td>
</tr>
<tr>
<td>5.</td>
<td>Timber from an old wooden house</td>
</tr>
<tr>
<td>6.</td>
<td>Painted veneer wood</td>
</tr>
<tr>
<td>7./8.</td>
<td>Upholstery from an old chair: Synthetic leather and foam (sponge)</td>
</tr>
<tr>
<td>9.</td>
<td>Old shoes</td>
</tr>
<tr>
<td>10.</td>
<td>Old newspapers</td>
</tr>
<tr>
<td>11.</td>
<td>Soil</td>
</tr>
</tbody>
</table>
2.2. Instrumentation

All samples were analysed using a Shimatzu GC 2010 gas chromatograph coupled with an MS QP 2010. The sample was introduced through a split/splitless injector, and 1 µl of sample was split 20:1 at a temperature of 275 °C using an auto-sampler. The chromatographic column was a TRB-1MS column of 0.25 mm internal diameter, 30 m length and 0.25 μm film thickness. Helium carrier gas was maintained at a flow rate 2.20 mL/min on the column. The initial oven temperature was held at 50 °C for 2.5 min, then ramped to 300 °C at a rate of 15°C/min and held for 5.83 min for a total run time of 25 min. The mass spectrometer was operated in the scan mode with a range from 40 to 500 m/z. The mass spectrometer transfer line was maintained at 210 °C with a source temperature at 200 °C. The chromatogram was operated with a solvent delay of 3.1 min. The detection limit of the GC-MS was determined by varying the concentration of petrol from 0.5 to 0.005 µl/mL. The detection limit was 0.05 µl/mL since at lower concentrations signal to noise ratio was less than three.

2.3. Petrol identification criteria

Samples of fresh petrol (0.5 or 1.0 µl/mL) in pentane were injected in the GC-MS. The different retention times for the major components were recorded. The identification of the different target molecules of petrol was done as per the criteria recommended by the American Society for Testing and Materials (ASTM) E 1618-06 [22]. The identity of each target compound was then confirmed by doing a similarity search of the mass spectrum of particular target compound against the reference library supplied with the GC-MS. The presence of petrol is characterized by an abundance of aromatic compounds whose peaks cluster in specific patterns within a carbon range of C4-C13, that is, the 4-peaks group of C3-alkylbenzenes (1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, 1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene and 1,2,4-trimethylbenzene) and the C2-alkylbenzenes (ethylbenzene and xylenes). The C4-alkylbenzenes namely the 1,2,4,5and 1,2,3,5-tetramethylbenzene must also be present to confirm the presence of petrol.

2.4. Evaluation of background interferences

Different selected substrates were cut into pieces (10 x 10 cm) except the soil sample. These substrates were subjected to analysis using passive headspace concentration [24]. The samples were placed horizontally in a nylon bag-11 type bags (obtained from BVDA NL) in order to produce a maximum volume. An activated charcoal strip (8 x 20 mm) obtained from the ACS (Albrayo Laboratories, Inc., Cromwell, CT), attached with a paper clip, was suspended in the headspace of the nylon bag above the substrate. The soil sample was placed in a petri dish before placing in the nylon bag. The bags were swan necked and sealed with cellotape and heated at 80 °C in an oven for 16 hours. The carbon strip was washed with pentane (2 x 2 mL) and the solvent was evaporated to 2 mL at room temperature and then transferred to auto-sampler vials for analysis by GC-MS.

The substrates (1-11) were burnt until half of the materials were consumed. The resulting debris were allowed to cool down and placed in nylon bag. The above experiment was repeated by using the partially burnt substrates.

2.5. Evaluation of the interfering products on the identification of petrol

Petrol (2 mL) was added to the substrates [1-11] and analysed with and without burning
Figure 1: Chromatogram of fresh unleaded petrol
Peak identities (1) toluene, (2) 2-methylheptane, (3) 3-methylheptane, (4) octane, (5) ethyl benzene, (6, 7) m/p xylenes, (8) o-xylene, (9) isopropylbenzene (10) propylbenzene, (11,12) 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene (13) 1,3,5-trimethylbenzene, (14) 1methyl-2-ethylbenzene, (15) 1,2,4-trimethylbenzene (16) 1,2,3-trimethylbenzene, (17) indane, (18) 1,2-dimethylethylbenzene (19) methylpropylbenzene (20) 1,2,4,5-tetra-methylbenzene, (21) 1,2,3,5-tetra-methylbenzene, (22) 1-methylnaphthalene; (23) 2-methylnaphthalene.

and subjected to analysis using passive headspace concentration. Neat petrol (2mL) was used as positive control. Carbon strips placed into empty nylon bags were analysed in between to ensure that the oven was not contaminated.

2.6. Evaporated samples

Petrol (4 ml) was evaporated by bubbling nitrogen gas and the volume was reduced to 3, 2, 1, 0.4 and 0.1 ml in order to attain 25, 50, 75 and 90 % evaporated sample. 0.5 µl/ml of the evaporated petrol in pentane was analysed. In order to obtain the 99 % evaporated sample, the petrol was left to evaporate for 5 days in the laboratory. The experiments were repeated five times.

2.7. Statistical validation

The linearity of the response of the detector and the reproducibility of the equipment were investigated by injecting 0.5 and 0.1 µl/mL of fresh petrol 5 times each. The retention times of the different target compounds were noted. The mean retention, relative standard deviation (RSD) values and confidence interval, were calculated for the different target compounds and are summarised in Table 2. The value of Student’s test was 2.262 for a 95% of confidence level [23].

The ratios of different isomers with similar vapour pressure were calculated for each run at different evaporation levels of the petrol samples. The average mean and the standard deviation of the different ratios were calculated. Box plots for the ratios were plotted to determine how the different ratios varies from the sample mean. The different ratios of the isomeric components were compared using one-way ANOVA.
3. Result and Discussion

3.1. Target peaks of petrol
The total ion chromatogram of fresh petrol in pentane was obtained by injecting 0.5 and 1 µL/mL of petrol in pentane in the GC-MS. Figure 1 is the chromatogram illustrating the major target compounds obtained for fresh petrol. The peaks due to naphthalene and methylnaphthalenes were detected when the conc. of fresh petrol was increased to 1.0 µL/mL (Figure 1). The petrol sample used in this study had only trace amount of alkylnaphthalenes. The relative amount of the poly-aromatic hydrocarbons in a particular petrol sample is dependent on the refining process and also on the degree of evaporation that occurs during post refinement both in storage and in use. The retention times of the different target compounds were noted and the RSD of the retention time was each peak was calculated noted. The low values of the RSD (1 <%) obtained within this study indicated the robustness and repeatability of the method [27].

3.2. Evaluation of the background and combustion products of substrate
Eleven different substances which are commonly found in the Mauritian environment were collected (Table 1) and the volatile compounds released by these substrates were identified and characterized. The volatile organic compounds from the partially burnt and unburnt materials were extracted and analysed using GC-MS.

It has been reported [1, 29] that cotton cloth gives rise to a number of interfering peaks, however in this study when cotton material was analysed the main background interference detected was toluene. This is most probably because the pretreatment processes of cloth are done differently locally.

The total ion chromatograms of burnt and unburnt used shoes showed toluene and a peak with retention time 6.78 min as the major interferences. Both signals were higher in the unburnt than in the burnt sample. Shoes are normally made up of polymer and uses adhesives during their manufacturing [1]. The background interferences may be due to either petroleum products that are held in the adhesive elastomeric matrix, and are released upon heating or any shoe polish that may have used. The peak at 6.78 min was attributed to a ketone, a component of sweat [30]. Sweat have been absorbed in the shoes and on heating the peak disappeared due to evaporation.

It is not unusual to find C3-and C4-alkylbenzenes, indanes, and naphthalenes in samples of burned carpet [14, 18]. However, the total ion chromatogram of the carpet analysed did not show any extraneous peaks in the region of petrol. In Mauritius, the carpets used are made up of naturally occurring material with no synthetic padding. This is may be the reason why the carpet, which was analysed in this study, gave different results than been reported elsewhere. The major interference observed in the extract of wood was toluene and it was of higher concentration in the unburnt as compared to the burnt sample. In addition to this, wood appears to have a few volatile components which may be due to C2 and C3 alkylbenzenes (4.75 & 6.50 min). The signals of these compounds were below the detection limit of accelerant and therefore the intensity was too low for meaningful interpretation. This is interesting, since in previous studies, it has been have reported that wood produces a number of products due to thermal degradation such as styrene and limonene [1, 31] but in this study less interfering products were obtained.
This may be due the fact that the type of timber in Mauritius is less resinous therefore fewer terpenes.

A number of volatile compounds including particularly toluene, C2 and C3 alkylbenzenes were detected in the extracts of new and old vinyl floorings and veneer painted wood. These peaks (3.5-10 min) appear in the same region as some of the hydrocarbons present in petrol. However the pattern being different from that of petrol can be differentiated (Figures 2a and 2b). 2-Ethyl-1-cyclohexanol (6.93 min) was another major interference in the vinyl samples and its concentration was higher in the burnt sample than in the unburnt sample but can be easily distinguished since it does not coelute with any petrol compounds. In addition, a series of peaks with retention times 10 -11 min were observed in the veneer painted wood sample. These extraneous peaks may be due to the petroleum products present in the paint [10]. The concentration of the more volatile residues including toluene was normally higher in the unburnt samples because on burning some of the petroleum products may have leached out.

The upholstery of chairs usually consists of the synthetic leather and sponge. At a fire scene, they are normally burnt together, however in this experiment the synthetic leather and the sponge were analysed separately. In the TIC of the extracts of the synthetic leather there were a series of peaks in the region of 4-8 min (Figure 2c). The synthetic leather is made up of polymeric materials and at high temperatures a number of compounds such as alkenes, and chloroalkanes are formed due to bond scission and reforming. These interfering products may represent potential problems in the interpretation of petrol due to co-elution of these products with compounds found in petrol. When the sponge material was tested, no extraneous peaks were observed except for a peak at 6.95 min corresponding to a pyrazolone derivative.

A series of aldehydic compounds were depicted as volatile background residues in the total ion chromatograms of burnt and unburnt newspaper. The toluene and an n-alkane series appearing at the back end of the chromatogram were most probably due to solvent added to the ink [1].

Soil is another common exhibit of fire cases. Its composition is influenced by microbial action [32]. The chromatogram of the unburnt soil sample showed toluene or hexanal and some peaks in the region of target molecules of petrol but the intensity of the peaks were below the detection limit for meaningful interpretation.
Characterisation of background and pyrolysis products

3.5

Figure 2: Chromatogram of (a) vinyl (b) veneer wood (c) synthetic leather
The different background and pyrolysis compounds identified from the substrates analysed are summarised in Table 2.

Table 2: Background hydrocarbons in substrates analysed.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Volatile Residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloth</td>
<td>Toluene</td>
</tr>
<tr>
<td>Shoes</td>
<td>Toluene, xylene, trimethylbenzene</td>
</tr>
<tr>
<td>Synthetic flooring</td>
<td>Toluene, C₃-alkylbenzene, methylheptane, branched cycloakane, C₈-alkenes, heptanone, C₉-aldehyde, octanol, ethylcyclohexanol</td>
</tr>
<tr>
<td>Carpet</td>
<td>-</td>
</tr>
<tr>
<td>Wood</td>
<td>Toluene, xylene, C₃-alkylbenzene</td>
</tr>
<tr>
<td>Painted veneer</td>
<td>Toluene, xylene, ethyltoluene, trimethylbenzene, C₈-ketone, C₈-alkane, pentadecane, esters</td>
</tr>
<tr>
<td>Synthetic leather</td>
<td>Hexanal, heptanone, octanal, ethyl hexanol, decanal, furan methanol</td>
</tr>
<tr>
<td>Foam</td>
<td>-</td>
</tr>
<tr>
<td>Soil</td>
<td>-</td>
</tr>
<tr>
<td>Newspaper</td>
<td>Toluene, caproaldehyde, heptanal, octanal, nonanal, &gt;C₂₀ alkanes</td>
</tr>
</tbody>
</table>

:-peaks too low

3.3 Influence of the interfering products on the identification of petrol

In the presence of cloth, vinyl flooring, wood, painted veneer wood, synthetic leather and sponge, the presence of petrol was easily depicted in both the unburnt and burnt sample by the presence of the C₂, C₃ and C₄-alkylbenzene patterns. In case of old vinyl flooring, the toluene peak was higher as compared to the other substrates since toluene was already present as an interfering product.
Comparison of the chromatograms of the burnt and unburnt extracts of shoes, carpet, newspaper and soil showed that significant amount of accelerant was consumed on burning. The burnt sample of shoes and soil samples showed only trace amount of petrol, however the presence of petrol was identified by the C2 and C3-alkylbenzenes pattern. The target compounds, methylheptane and octane found at the front end of the chromatogram were absent in the burnt sample since during burning, low molecular weight compounds had evaporated. However, the toluene peak is enhanced in the shoe extract as it is an interfering product and has added up to the remaining toluene of the accelerant after burning. The interference peak with retention time at 6.775 min due to sweat was present only in the unburnt sample of shoes.

The presence of petrol could not be identified in the extract of burnt carpet and newspaper as the characteristic patterns of petrol corresponding to the C2 and C3-alkyl benzenes were missing (Figure 3a & 3b). In the case of newspaper, peaks corresponding to medium and heavy petroleum distillates were due to as background interference since they were also identified when newspaper was analysed in the absence of petrol.

In the control experiments petrol was inserted either directly or was placed in a petri-dish before placing it into the nylon bag. When petrol was directly inserted into the nylon bag, toluene, the C9-alkanes and the C2-alkylbenzenes were absent in the TIC (Figure 4). This may be due to loss of the more volatile residues by evaporation or the latter leaked out at a higher rate when in direct contact of the plastic. This could result in cross-contamination of samples as there can be transfer of hydrocarbons from one closed container to another and it also shows that nylon bags cannot be used as evidential container of neat accelerant. This is an interesting observation as this result has not been reported previously and indicates a significant effect in analysis particularly for contamination problems for forensic samples.

![Figure 3: Chromatogram of burnt (a) carpet (b) newspaper in the presence of petrol.](image)

![Figure 4: Chromatograms of fresh petrol (a) inserted directly in nylon bag (b) in a petridish](image)
3.7 Influence of weathering on petrol

As the degree of weathering increases, the more volatile hydrocarbons are lost more easily. These losses are neither linear nor constant throughout the vapour pressure range in petrol. However the relative ratios of the isomeric compounds are comparable [32]. The different ratios (ratio 1: m/p-xylene/ethyl benzene; ratio 2: o-xylene/ethyl benzene; ratio 3: 1,2,4-trimethylbenzene/1,3,5-trimethylbenzene; ratio 4: 1,2,3,5-trimethylbenzene/1,2,4,5-trimethylbenzene; and ratio 5: 2-methylnaphthalene/1-methylnaphthalene) were calculated. The box plots of the different ratios (1-5) illustrate reproducibility within a sample (Figure 5). For the 90% evaporation, the ratios showed highest fluctuations around the mean value as compared to the other levels of evaporation. This is due to the fact that the volume was read with less accuracy. For 25-75 % evaporation samples, the ratio 3 had more fluctuations among the replicates. The ratios 1, 2, 4 and 5 showed less fluctuation around their mean values. The value of the ratios for the different isomers were compared for each sample and they were found to be within 5% standard deviation except for the ratio 3 and those for 90 % evaporated samples.

![Figure 5: Boxplots of the ratios (1-5) of the different components illustrating reproducibility within a sample at various levels of evaporation.](image)

For the 25 and 50 % evaporated samples, the relative ratios (1-5) had P > 0.050, therefore the relative ratios cannot be used to differentiate between these two evaporated samples. The relative ratios of C3-alkylbenzences (ratios 1 and 2) can be used to differentiate the 25 and 75% evaporated samples at 95% confidence limit as the mean ratios were significantly different(P< 0.05). The ratios 3, 4 and 5 were significantly different for the 25 and 90 % evaporated samples. Considering the ratios 1, 2, 4 and 5, it was found that the different levels of evaporation can be determined at 95 % confidence limit. This comparison method is useful as gives some idea
about the degree of weathering of petrol and whether the petrol found on a fire scene was a contaminant or freshly spilled.

3. Conclusion

Background interferences depend on the origin of substrates. The common background hydrocarbons which may interfere with the identification of petrol are toluene, xylene, alkylbenzenes, alkanes and alkenes. The presence of these products is not always constant but depends on the provenance of the substrate, thus, making it difficult to extrapolate data from similar cases. This highlights the importance of analysing control samples in fire debris analysis in order to differentiate background hydrocarbons and accelerant hydrocarbons.

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