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## Effect of evaporation and matrix interferences on the association of simulated ignitable liquid residues to the corresponding liquid standard<sup>☆</sup>

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### ARTICLE INFO

#### Article history:

Received 23 December 2011

Received in revised form 10 May 2012

Accepted 1 June 2012

Available online 22 June 2012

#### Keywords:

Ignitable liquids

Gas chromatography–mass spectrometry

Matrix interferences

Pearson product moment correlation

Hierarchical cluster analysis

Principal components analysis

### ABSTRACT

Identification of an ignitable liquid in fire debris evidence can be complicated due to evaporation of the liquid, matrix interferences, and thermal degradation of both the liquid and the matrix. In this research, liquids extracted from simulated fire debris were compared to the original liquid using multivariate statistical procedures. Neat and evaporated gasoline and kerosene standards were spiked onto nylon carpet, which was subsequently burned. The ignitable liquid residues were extracted using a passive headspace procedure and analyzed by gas chromatography–mass spectrometry. Pearson product moment correlation coefficients, hierarchical cluster analysis, and principal components analysis were used to compare the liquids extracted from the carpet to the corresponding neat liquid. For each procedure, association of the extracts according to liquid type was possible, albeit not necessarily to the specific evaporation level. Of the three procedures investigated, principal components analysis offered the most promise since contributions from matrix interferences were essentially eliminated.

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### 1. Introduction

Debris collected at the site of suspicious fires is extracted and analyzed by gas chromatography–mass spectrometry (GC–MS) to determine the presence of extraneous ignitable liquid residues (ILRs). The total ion chromatogram, as well as extracted ion profiles of selected compound classes, can then be compared to a reference collection of ignitable liquids to identify any ILR present. However, the identification is complicated by a number of factors including evaporative losses of the liquid and the presence of matrix interferences, as well as the procedure used to extract the liquid from the matrix. Due to the heat of the fire, the more volatile compounds in the ignitable liquid evaporate, which changes the chemical composition of the liquid. As such, the chromatogram of an evaporated liquid can be visually very different from that of the original, unevaporated liquid. Hydrocarbons or petroleum-based products inherent in the debris, as well as those produced through thermal degradation of the debris, can also introduce matrix interferences in the chromatogram of the extracted ILR. Differences in the procedure used to extract the liquid from the matrix

compared to that of the reference standard may also result in differences in the chromatograms.

To address problems associated with evaporation and matrix interferences, the reference collection to which the chromatogram of the ILR is compared may be expanded to include chromatograms of liquid standards evaporated to different levels, as well as chromatograms of unburned and burned household matrices. While this enables identification of the source of some additional peaks in the chromatogram of the fire debris, visual comparison of chromatograms remains complicated.

With the publication of the National Academy of Sciences, National Research Council report, '*Strengthening Forensic Science in the United States: A Path Forward*,' there has been growing awareness of the need for statistical evaluation of forensic evidence [1]. Such evaluation would be ideal in fire debris analysis to provide an objective decision-making tool to assess the association of questioned samples to reference standards. These procedures provide a quantitative statistical assessment of the comparison, which is not possible based on a visual assessment of chromatograms.

Lennard et al. developed a method for the identification of ignitable liquids in fire debris samples based on the presence of target compounds in the chromatograms [2]. A range of different liquids was analyzed in the unevaporated state, after evaporation to different levels, and after extraction from a range of substrates that had been spiked with the liquids and burned. The retention time and relative abundance of the most abundant two or three

<sup>☆</sup> This work was partially funded by the Midwest Forensics Resource Center (Prime Contract No. DE-AC02-07CH11358) and was presented at the 63rd American Academy of Forensic Sciences Annual Meeting (Chicago, IL, February 2011).

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ions in 40 target compounds were determined and stored in a database for comparison purposes. The method was successfully applied in a casework sample that contained gasoline. Analysis of this sample using gas chromatography with a flame ionization detector had previously proved inconclusive. Using the target compound approach, weathered gasoline was identified in the sample and confirmed through comparison to a 90% evaporated gasoline sample. However, this procedure requires generation of target compounds for each class of ignitable liquids and hence, *a priori* knowledge of the liquid expected in any sample is necessary such that the correct target compounds can be used for comparison.

Since each chromatogram is composed of hundreds, if not thousands, of variables, multivariate statistical procedures offer an efficient means to evaluate chromatograms in a more quantitative manner. Procedures such as principal components analysis (PCA), linear discriminant analysis (LDA), and artificial neural networks (ANNs) have previously been used to assess association and discrimination of gasoline samples [3–7]. These investigations have included association of evaporated gasoline to the corresponding unevaporated gasoline [6]. However, selected peaks or sections of the chromatogram were used in these studies, rather than the full chromatogram, potentially limiting the discriminating information available.

Potential interferences from a variety of common household matrices have also been investigated and reported in the literature [8–11]. Both unburned and burned matrices have been extracted and analyzed to identify interferences inherent to the matrix, as well as those introduced as a result of thermal degradation or pyrolysis. However, in these studies, matrices were burned in the absence of any ignitable liquid.

In spite of this previous research, there are few studies in the literature that consider the association and discrimination of liquids in the presence of both evaporative losses and matrix interferences [12–14]. Bertsch reported that pyrolysis products from burned carpet, such as alkylbenzenes and naphthalenes, could interfere with the identification of gasoline [12]. However, using selected ion monitoring, sufficient differences were apparent between the burned matrix and the liquid to enable the distinction and identification of gasoline. Borusiewicz et al. studied the effects of liquid type, matrix type, burn time, and air availability on the detection of five different types of ignitable liquid using GC–MS [13]. In both of these studies, comparisons were based on visual assessment of chromatograms and no statistical comparisons were reported.

Tan et al. used PCA and a soft independent modeling of class analogy (SIMCA) approach to classify 51 ignitable liquids according to classes defined by the American Society for Testing and Materials (ASTM) [14]. Liquids were then spiked onto carpet and burned to simulate fire debris. Ignitable liquid residues were extracted from the matrix using a solvent extraction procedure, rather than the passive headspace extraction procedure more commonly employed in forensic laboratories. Extracts were analyzed using GC–MS in the selected ion monitoring mode to minimize contributions from matrix interferences. Subsequent data analysis was based on a condensed version of each chromatogram, based on 19 variables, rather than the full chromatogram. While all simulated ILRs were successfully classified using SIMCA, no discussion of the matrix interferences was included.

Baerncof et al. used PCA and Pearson product moment correlation (PPMC) coefficients to compare simulated ILRs to the corresponding neat liquid [15]. One liquid from each of six ASTM classes was spiked onto separate pieces of nylon carpet that were subsequently burned. Both light and heavy burning conditions were investigated although, in both cases, the spiked liquid

dominated the resulting chromatogram. Successful association of each ILR to the corresponding neat liquid was demonstrated. A second liquid standard from each of the six ASTM classes was added to the sample set and the statistical procedures repeated. Residues containing liquids in the gasoline and petroleum distillates classes could only be identified by class, rather than actual liquid type, due to the similarity in chemical composition of the liquids in these classes.

In the proof-of-concept study reported herein, a combination of multivariate statistical procedures is used to compare simulated ILRs to the corresponding liquid in the presence of both evaporative losses and matrix interferences. Gasoline and kerosene were selected as the model liquids due to their wide availability and common use in intentional fires. A set of liquid standards containing neat and evaporated gasoline and kerosene was firstly prepared. Association of the evaporated liquid to the corresponding neat liquid was investigated using PPMC coefficients, hierarchical cluster analysis (HCA), and PCA. These procedures were chosen since *a priori* knowledge of the samples is not required. Correlation coefficients measure similarity between two samples and may be useful in a forensic laboratory for the comparison of a questioned sample to a known reference sample. In HCA, similarity is also measured; however, in contrast to PPMC coefficients, multiple samples are considered simultaneously rather than in a pair-wise manner. This is also true in PCA; however, variance, rather than similarity, is measured. Both HCA and PCA could be useful in a forensic laboratory to compare a questioned sample to a set of reference standards.

In all cases, statistical procedures were performed on the full chromatogram rather than on peak ratios, selected sections of the chromatogram, or extracted ion chromatograms. The full chromatogram (*i.e.*, every time point) was used to avoid eliminating potentially useful variables that would allow association and discrimination of the standards and simulated ILRs. Additionally, using the full chromatogram removes any subjectivity associated with the selection of appropriate variables for subsequent data analysis procedures.

Each liquid standard was spiked onto a nylon carpet matrix that was subsequently burned to simulate fire debris. The burn time was previously investigated to ensure the maximum number and abundance of interferences. The chromatograms resulting from the simulated debris were subjected to the same statistical procedures to investigate association of the extract to the corresponding liquid standard, in the presence of both evaporative loss and matrix interferences.

## 2. Experimental

### 2.1. Preparation of liquid standards

Gasoline and kerosene were purchased from a local gas station and stored in acid-washed amber bottles in the refrigerator until analysis. Gasoline was evaporated to 10% and 90% (v/v) under a stream of purified air, while kerosene was evaporated to 10% and 70% (v/v) in a similar manner. These evaporation levels were chosen to allow investigation of the effects of minimal evaporation compared to substantial evaporation on association of the samples to the liquids. Since kerosene contains compounds that are less volatile than those in gasoline, evaporation to 70% (v/v) was sufficient to observe noticeable changes in chemical composition. The neat and evaporated liquids were diluted 1:25 (v/v) in dichloromethane (Spectrograde, Jade Scientific, Canton, MI) containing 0.03 M nitrobenzene (Mallinckrodt, Paris, KY) as an internal standard. Each liquid was spiked (20  $\mu$ L) onto a separate Kimwipe™ and placed in a nylon bag (Grand River Products, Grosse Pointe Farms, MI). An activated carbon strip (2.5 mm  $\times$  5 mm, Albrayco Laboratories, Cromwell, CT) was also suspended in the nylon bag using a paper clip that had been pre-rinsed in dichloromethane. The bags were sealed with general purpose masking tape (Duck Products, Avon, OH) and placed in an oven at 80 °C for 4 h, in accordance with procedures recommended by ASTM International [16]. All standards and samples were prepared using the same extraction procedure to minimize differences in the resulting chromatograms attributable to the extraction procedure. Following extraction, the carbon strip was eluted with 200  $\mu$ L of dichloromethane and the extract was then analyzed by GC–MS.

A consensus standard, which was necessary for retention time alignment, was prepared in dichloromethane and contained neat gasoline (1:25, v/v) and neat kerosene (1:25, v/v). The standard was spiked onto a single Kimwipe™ in a nylon bag, then extracted as described above and analyzed by GC–MS.

## 2.2. Investigation of matrix interferences from nylon carpet

Nylon carpet (source and monomer composition unknown) was cut into 4 cm × 4 cm pieces that were burned using a propane blowtorch for burn times of 0, 10, 20, 30, 60, and 120 s. After the specified time had elapsed, a beaker was placed over the burning matrix to extinguish the flame. The burned carpet pieces were placed in separate nylon bags, each containing an activated carbon strip. The bags were sealed and placed in an oven at 80 °C for 4 h, as described above. Following extraction, the carbon strip was eluted with 200 µL of dichloromethane and the extract was then analyzed by GC–MS.

## 2.3. Preparation of simulated ILRs

Additional 4 cm × 4 cm samples of nylon carpet were prepared and five such samples were burned for 60 s to serve as control samples. Each liquid standard was then spiked onto a separate carpet sample. A 750-µL aliquot of each gasoline standard was spiked while a 250-µL aliquot of each kerosene standard was spiked. These volumes were determined in preliminary studies to ensure that the liquid did not dominate the resulting chromatograms. This procedure was repeated to generate a total of five spiked carpet samples for each liquid standard. The carpet samples were then burned for 60 s and extinguished, following the procedures described above.

The burned samples were placed in separate nylon bags with an activated carbon strip and extracted at 80 °C for 4 h, as described previously. After extraction, the carbon strips were eluted with 200 µL of dichloromethane and analyzed by GC–MS.

## 2.4. GC–MS analysis

All extracts were analyzed using an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a DB-5 ms column (0.25 mm × 30 m × 0.25 µm, Agilent Technologies, Palo Alto, CA). Ultra-high purity helium was used as the carrier gas with a nominal flow rate of 1 mL/min. The inlet was maintained at 250 °C and an Agilent 7683B automated liquid sampler (Agilent Technologies) was used to inject 1 µL of extract in pulsed splitless mode, using a pulse of 15 psi for 0.25 min. The oven temperature program was based on the program used by the National Center for Forensic Science: 40 °C for 3 min, 10 °C/min to 280 °C, with a final hold of 4 min [17]. The transfer line to the Agilent 5975 mass selective detector (Agilent Technologies) was maintained at 280 °C. Electron ionization (70 eV) was used and the quadrupole mass analyzer was operated in the full scan mode ( $m/z$  50–550) with a scan rate of 2.91 scans/s. All extracts were analyzed in triplicate.

## 2.5. Data pretreatment and analysis

Total ion chromatograms for the liquids and extracts were generated in ChemStation software (version E.01.01.335, Agilent Technologies) and compounds in each extract were identified through comparison of mass spectral data with the NIST Mass Spectral Search Program (version 2.0d, National Institute of Standards and Technology, Gaithersburg, MD).

Prior to data analysis, the chromatograms were subjected to several preprocessing steps to minimize non-chemical sources of variance. The first step involved removing the caprolactam peak in each chromatogram. Since caprolactam is a component of the nylon bags, background subtraction was necessary to remove the irreproducible contribution that would otherwise introduce variance into the data set. Background correction was performed using the appropriate function in the ChemStation software. Each chromatogram was then smoothed using a Savitzky–Golay algorithm, a function also available in the ChemStation software.

The chromatograms were retention-time aligned using a correlation optimized warping algorithm (LineUp™, version 3.0, Infometrix, Bothell, WA) with a warp of 2 data points and a segment size of 75 data points. Finally, the chromatograms were normalized in two stages: firstly to the internal standard, followed by total area normalization of the full data set. Normalization to the internal standard was used to ensure that the abundance of the maximum peak in each chromatogram was on the same order of magnitude, while total area normalization was used to minimize spread among replicates due to differences in injection volume. For internal standard normalization, the abundance at each retention time was initially divided by the abundance of the internal standard in the chromatogram. Then, for total area normalization, the area of each chromatogram in the data set was summed and the average area of all chromatograms was calculated. The abundance at each retention time was then divided by the area of that chromatogram and multiplied by the average area of all chromatograms. All normalization calculations were performed in Microsoft Excel (Excel 2007, Microsoft, Redmond, WA).

Pearson product moment correlation (PPMC) coefficients were also calculated in Microsoft Excel for pair-wise comparisons of all chromatograms. The coefficient,  $r$ , ranges from +1 to –1, with a positive coefficient indicating positive correlation

between two samples and negative coefficient indicating negative correlation [18]. Coefficients between ±0.8 and ±1 indicate strong correlation, between ±0.5 and ±0.79 indicate moderate correlation, and less than ±0.5 indicate weak correlation. Coefficients close to zero indicate no correlation. Correlation coefficients among replicates were used to assess precision in the extraction and analysis procedures. Coefficients among standards and extracts were used to assess correlation among liquid standards and simulated ILRs.

The pretreated data were subjected to hierarchical cluster analysis (HCA), which was performed in Pirouette (version 4.0, Infometrix) using the Euclidean distance measurement and the central linkage method. Cluster analysis was initially performed on the chromatograms of the liquid standards alone to assess grouping of the evaporated liquids and corresponding neat liquids. The analysis was then repeated, this time including chromatograms for liquids extracted from the burned carpet matrix, to assess association of the simulated ILR to the corresponding neat liquid. In each case, dendrograms were generated to assess similarity among the liquid standards and ILRs based on the similarity index, which is a measure of the similarity of samples relative to the full data set.

Principal components analysis (PCA) was then performed on the data using Matlab (version R2010b, The Mathworks, Natick, MA). Eigenvectors and eigenvalues were generated for the liquid standards only and the scores and loadings plots were generated in Microsoft Excel. Data for the simulated ILRs were then mean centered to the liquid standards, and scores for each ILR were calculated using the eigenvectors previously generated. The calculated scores for the ILRs were projected onto the original scores plot to assess association of the ILRs to the corresponding liquid standard. Projecting scores in this way ensures that similarities and differences between the simulated ILRs and standards are chemical in nature, rather than artifacts of the burning and extraction processes.

## 3. Results and discussion

### 3.1. Effect of evaporation on chemical composition of liquids

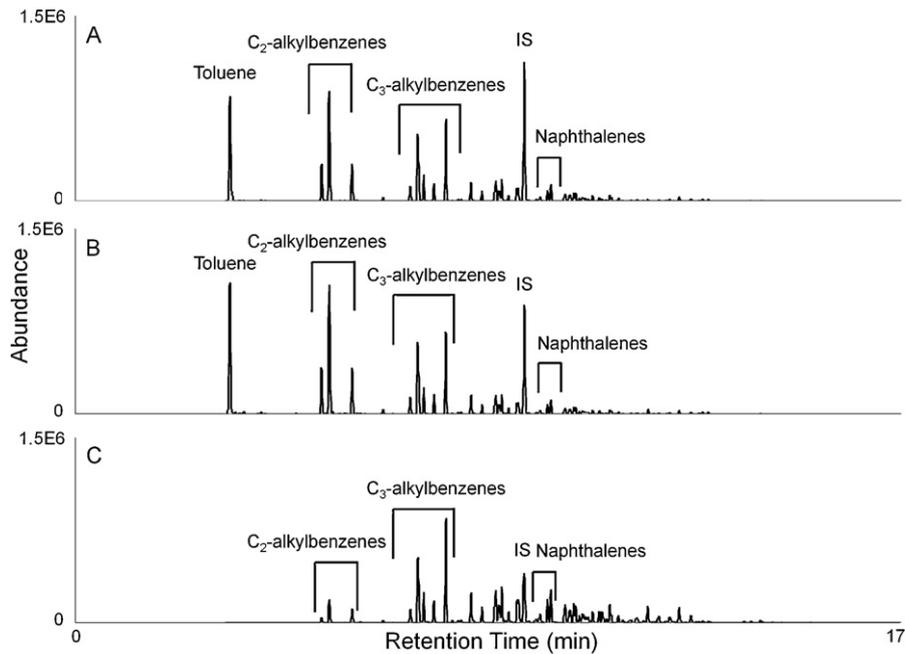
Exemplar chromatograms of gasoline and kerosene at each evaporation level are shown in Figs. 1 and 2, respectively. The chromatogram of neat gasoline is dominated by toluene, the C<sub>2</sub>-alkylbenzenes, and the C<sub>3</sub>-alkylbenzenes, with additional contributions from the C<sub>4</sub>-alkylbenzenes and the methylnaphthalenes. At the 90% evaporation level, toluene has been lost, while the C<sub>2</sub>-alkylbenzenes are substantially lower in concentration. In contrast, the less volatile compounds (*i.e.*, C<sub>3</sub>-alkylbenzenes, C<sub>4</sub>-alkylbenzenes, and the methylnaphthalenes) have become more concentrated.

The chromatogram for neat kerosene is dominated by the C<sub>11</sub>–C<sub>16</sub> normal alkanes, with aromatic compounds present at low abundance early in the chromatogram. As evaporation level increases, these aromatic compounds, along with the C<sub>10</sub> and C<sub>11</sub> normal alkanes are lost, the abundance of the C<sub>12</sub> and C<sub>13</sub> alkanes is reduced, and the C<sub>14</sub>–C<sub>16</sub> alkanes become more concentrated. As a result, the distribution and the ratios of the normal alkanes change due to evaporative losses.

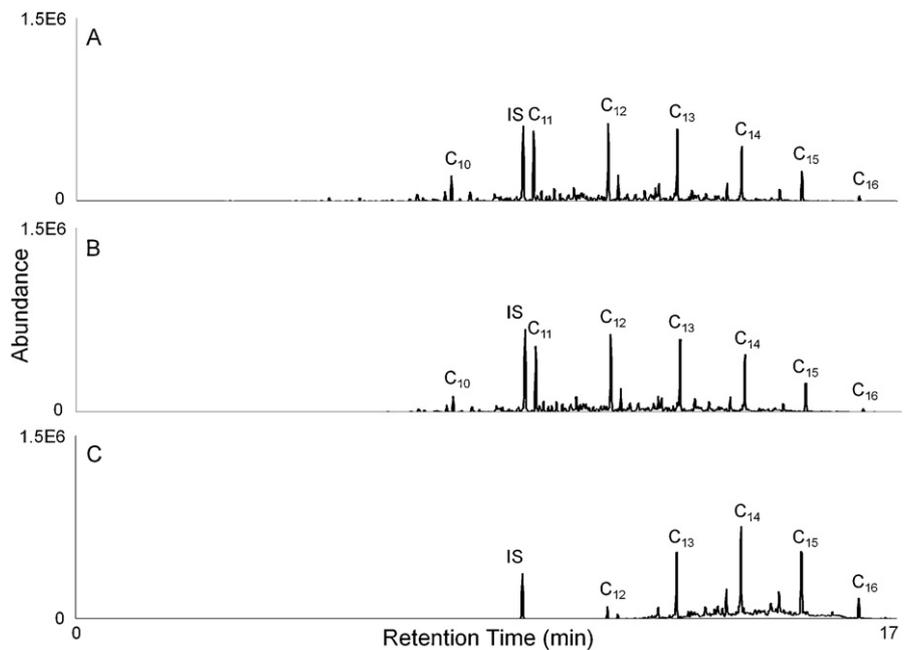
### 3.2. Effect of evaporation on association of liquids using PPMC coefficients

Mean PPMC coefficients were calculated for replicates ( $n = 15$ ) of each ignitable liquid standard, and are shown along the diagonal in Table 1. In all cases, the mean PPMC coefficients are greater than 0.986, which indicates strong correlation among replicates, as expected. In addition, standard deviations are less than 0.012, which indicates acceptable precision in the extraction and analysis procedures.

Mean PPMC coefficients comparing the neat and evaporated standards are also shown in Table 1. For gasoline, strong correlation is observed between the neat and 10% evaporated standards, despite lower abundance of toluene and the C<sub>2</sub>-alkylbenzenes in the evaporated standard (Fig. 1). Pearson product moment correlation coefficients are calculated based on a point-by-point comparison of the data and, although sensitive to relative differences in abundance, the coefficients are insensitive to overall differences in abundance. Thus, despite differences in abundance



**Fig. 1.** Exemplar total ion chromatograms of (A) neat gasoline, (B) 10% evaporated gasoline, and (C) 90% evaporated gasoline standards. Note that “IS” indicates internal standard, which in this case was nitrobenzene.



**Fig. 2.** Exemplar total ion chromatograms of (A) neat kerosene, (B) 10% evaporated kerosene, and (C) 90% evaporated kerosene standards. Note that “IS” indicates internal standard, which in this case was nitrobenzene.

**Table 1**

Mean Pearson product moment correlation (PPMC) coefficients  $\pm$  one standard deviation for replicates ( $n = 105$ ) of each ignitable liquid standard (shown in the diagonal) as well as among standards ( $n = 225$ ).

Mean PPMC coefficient $\pm$ standard deviation						
	Neat gasoline	10% evaporated gasoline	90% evaporated gasoline	Neat kerosene	10% evaporated kerosene	70% evaporated kerosene
Neat gasoline	0.986 $\pm$ 0.012					
10% evaporated gasoline	0.988 $\pm$ 0.011	0.992 $\pm$ 0.006				
90% evaporated gasoline	0.628 $\pm$ 0.032	0.624 $\pm$ 0.03	0.996 $\pm$ 0.002			
Neat kerosene	0.304 $\pm$ 0.045	0.290 $\pm$ 0.035	0.395 $\pm$ 0.015	0.994 $\pm$ 0.005		
10% evaporated kerosene	0.25 $\pm$ 0.04	0.236 $\pm$ 0.033	0.338 $\pm$ 0.013	0.989 $\pm$ 0.005	0.994 $\pm$ 0.004	
70% evaporated kerosene	0.109 $\pm$ 0.023	0.102 $\pm$ 0.018	0.104 $\pm$ 0.007	0.608 $\pm$ 0.012	0.641 $\pm$ 0.013	0.994 $\pm$ 0.004

between the neat and 10% evaporated standards, the same compounds are present, resulting in strong correlation. In contrast, only moderate correlation is observed for comparisons of the 90% evaporated gasoline standard to the neat and 10% evaporated standard due to the lack of toluene in the 90% standard. The same general trend is observed for the kerosene standards for similar reasons; that is, the evaporative loss of the early-eluting aromatic compounds, along with C<sub>10</sub> and C<sub>11</sub>, in the 70% evaporated standard compared to the neat and 10% evaporated standards.

When PPMC coefficients are compared between gasoline and kerosene, there is only weak correlation (<0.4) for all combinations (Table 1). Consequently, differentiation of gasoline and kerosene is possible at all levels of evaporation, as expected due to the significant differences in chemical composition between the two liquid types.

### 3.3. Effect of evaporation on association of liquids using HCA

The HCA dendrogram generated for the liquid standards, using the Euclidean distance measurement and the complete linkage method, is shown in Fig. 3. As expected, there is no similarity (similarity index = 0) between the gasoline standards and the kerosene standards. For gasoline, the neat and evaporated standards have a similarity index of only 0.26; however, this low similarity is expected due to the significant difference in composition of the 90% evaporated standard.

The neat and 10% evaporated gasoline standards form one group and have a similarity index of 0.71. Initially, this index seems rather low, considering the similarity in the chromatograms of these two standards (Fig. 1) and the strong correlation indicated by the PPMC coefficient ( $0.988 \pm 0.011$ ). These apparent discrepancies are due to differences in the statistical procedures: in HCA, similarity of samples is calculated relative to all samples in the data set (in this case, both gasoline and kerosene), while PPMC coefficients are calculated for only two samples at a time. Replicates of the 90% evaporated standard form a distinct group and have a similarity index of 0.88. This greater similarity is due to the loss of the more volatile, and hence, variable, compounds as evaporation level increases.

The neat and evaporated kerosene standards have a similarity index of 0.51. The higher similarity among standards compared to the gasoline standards is expected as kerosene contains fewer

volatile compounds and, in this study, is only evaporated to 70% (v/v) compared to 90% (v/v) for gasoline. Since there is little difference in chemical composition between the neat and 10% evaporated kerosene (Fig. 2), replicates of these standards form one group with a similarity index of 0.84. Replicates of the 70% evaporated kerosene form a distinct group and have a similarity index (0.91) that is greater than that of the neat and 10% evaporated standards. Again, due to evaporation, the more volatile and variable compounds are lost, increasing the similarity among replicates of the most evaporated standard.

Thus, using HCA, the gasoline and kerosene standards are easily differentiated. For each liquid, the neat and 10% evaporated standards have similar chemical composition and are clustered together, while the most evaporated standard forms a unique cluster, due to distinct differences in chemical composition.

### 3.4. Effect of evaporation on association of liquids using PCA

The PCA scores plot based on the liquid standards is shown in Fig. 4. The first two principal components (PC1 and PC2) account for 87.7% of the total variance. Replicates of each liquid are closely associated, indicating acceptable precision in the extraction and analysis procedures, as previously indicated using PPMC coefficients. The first principal component distinguishes the liquids, with the gasoline standards positioned negatively and the kerosene standards positioned positively on this PC. The actual position of the liquids on the scores plot can be explained with reference to the loadings plots for PC1 and PC2, which are shown in Fig. 5.

From the loadings plots, toluene, C<sub>2</sub>-alkylbenzenes, and C<sub>3</sub>-alkylbenzenes are weighted negatively on PC1 (Fig. 5A). Since these are the dominant compounds in gasoline, the gasoline standards are positioned negatively on PC1 in the scores plot. Furthermore, at the 90% evaporation level, toluene is lost. Hence, for the 90% evaporated gasoline standard, there is less negative contribution on PC1 such that this standard is positioned closer to zero than the neat and 10% evaporated gasoline standards in the scores plot.

The C<sub>10</sub>–C<sub>16</sub> normal alkanes, which are the dominant compounds in kerosene, are weighted positively on PC1, with greater contribution from the C<sub>12</sub>–C<sub>14</sub> alkanes. As a result, the kerosene

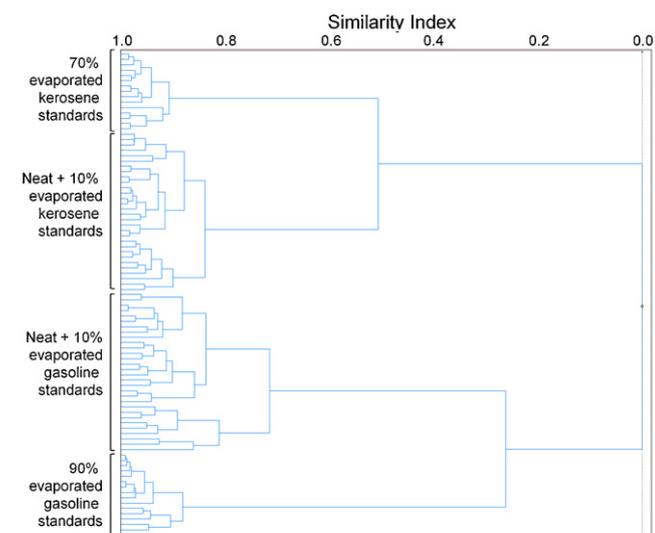


Fig. 3. Dendrogram generated for gasoline and kerosene standards using hierarchical cluster analysis, with Euclidean distance measurement and complete linkage method.

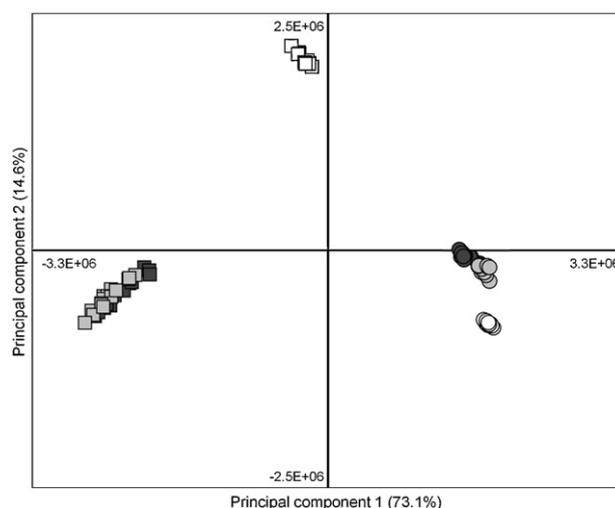
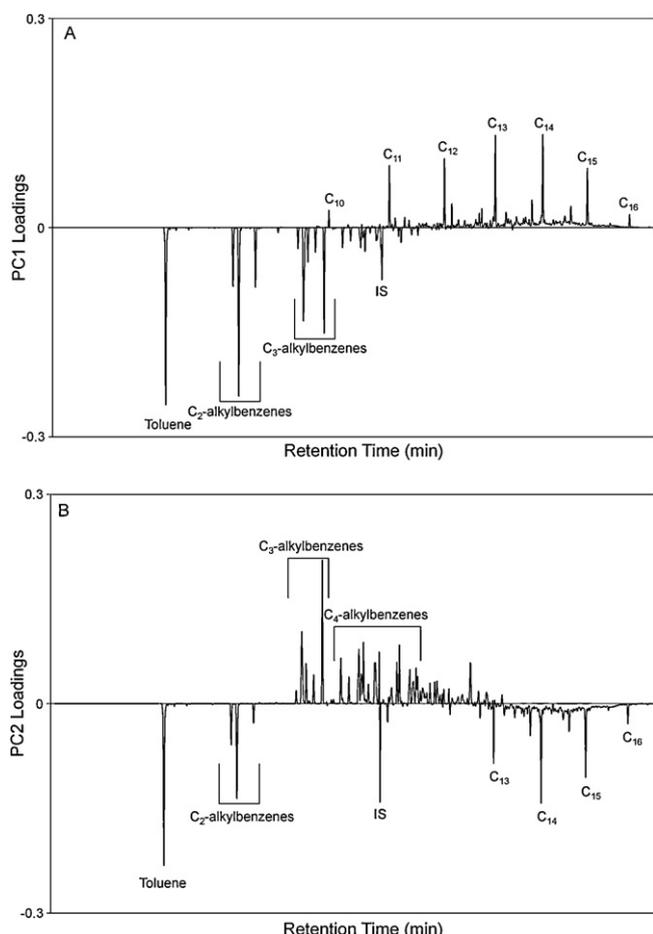


Fig. 4. Scores plot of principal component 1 versus principal component 2 for neat and evaporated gasoline and kerosene standards. Each liquid was extracted in replicate ( $n = 5$ ) and each extract was analyzed in triplicate, resulting in a total of 15 data points for each liquid in the scores plot. Each standard is denoted as follows: neat gasoline (■), 10% evaporated gasoline (□), 90% evaporated gasoline (□), neat kerosene (●), 10% evaporated kerosene (○), and 70% evaporated kerosene (○).



**Fig. 5.** Loadings plot for (A) principal component 1 and (B) principal component 2 based on the scores plot for the gasoline and kerosene standards shown in Fig. 4.

standards are positioned positively on PC1 in the scores plot. These normal alkanes are relatively unaffected by the evaporation process due to their low volatility, even at the 70% evaporation level. Hence, the neat and evaporated kerosene standards are positioned closely on PC1 in the scores plot.

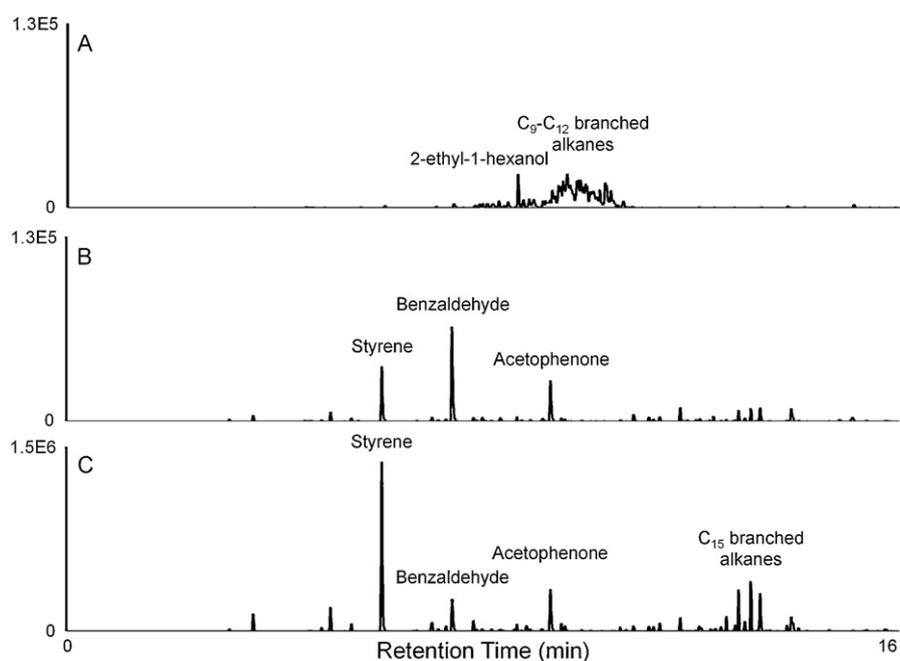
Toluene, C<sub>2</sub>-alkylbenzenes, and the C<sub>13</sub>–C<sub>16</sub> normal alkanes are weighted negatively on PC2, whereas the C<sub>3</sub>-alkylbenzenes and C<sub>4</sub>-alkylbenzenes are weighted positively (Fig. 5B). Due to the higher abundance of toluene and C<sub>2</sub>-alkylbenzenes, compared to the C<sub>3</sub>-alkylbenzenes, in the neat and 10% evaporated gasoline standards, these standards are positioned negatively on PC2 in the scores plot. However, the 90% evaporated gasoline standard contains no toluene, a lower abundance of the C<sub>2</sub>-alkylbenzenes, and a higher abundance of the C<sub>3</sub>-alkylbenzenes (Fig. 1). As a result, the 90% evaporated gasoline standard is positioned positively on PC2 in the scores plot, due to the greater contribution of the positively weighted C<sub>3</sub>-alkylbenzenes.

The C<sub>13</sub>–C<sub>16</sub> normal alkanes that are present in the kerosene standards are weighted negatively on PC2 (Fig. 5B). Due to their low volatility, these alkanes are not significantly affected by the evaporation process. Hence, the neat, 10% evaporated, and 70% evaporated kerosene standards are all positioned negatively on PC2 in the scores plot. The 70% evaporated standards are positioned most negatively on this PC since the normal alkanes are present in greatest abundance in this standard, as a result of the evaporation process.

Using PCA, differentiation of the liquid standards according to type is possible on the first PC. In addition, for both liquid types, the second PC differentiates the most evaporated standard as a result of the substantial differences in chemical composition occurring during evaporation.

### 3.5. Investigation of interference effects from carpet

Exemplar chromatograms of the nylon carpet burned for 0, 30, and 60 s are shown in Fig. 6. With no burning (Fig. 6A), the inherent interferences are C<sub>9</sub>–C<sub>12</sub> branched alkanes and 2-ethyl-1-hexanol, which likely originate from the adhesive, the yarn, and the backing material of the carpet. With a burn time of 30 s (Fig. 6B), styrene,



**Fig. 6.** Exemplar total ion chromatograms of nylon carpet burned for (A) 0 s, (B) 30 s, and (C) 60 s.

benzaldehyde, and acetophenone dominate the chromatogram, with C<sub>15</sub> branched alkanes also present at low abundance. These compounds were also identified by Furton and Almirall in nylon carpet samples after burning and are likely present due to thermal degradation of the carpet [8]. Since the exact composition of the carpet is unknown, the origin of these interference compounds is unclear; however, styrene is generated *via* side group scission of polymers such as polyvinyl chloride during pyrolysis [19].

At 60 s (Fig. 6C), there is a significant increase in matrix interferences, with styrene dominating the chromatogram and greater contribution from the C<sub>15</sub> alkanes. As the burn time increased further to 120 s, there were no additional matrix interferences and, hence, 60 s was chosen as the burn time for all subsequent studies.

### 3.6. Association of simulated ILRs to liquid standards using PPMC coefficients

Exemplar chromatograms of the simulated ILRs containing neat gasoline and neat kerosene are shown in Fig. 7. While the major compounds of the liquids are still visible, there are additional contributions from the matrix that make association to the corresponding standards (Fig. 1), based on visual assessment, more difficult. Hence, each of the afore-mentioned statistical procedures was applied to compare the simulated ILRs to the appropriate liquid standard.

PPMC coefficients were calculated for pair-wise comparisons of replicates of the simulated ILRs (Electronic Supplementary Material, Table 1). For both gasoline- and kerosene-containing ILRs, coefficients are generally greater than 0.9, indicating strong correlation among replicates and, hence, acceptable precision in the extraction and analysis procedures. There are two exceptions to this: the 90% evaporated gasoline ILRs, for which the mean PPMC coefficient is  $0.698 \pm 0.295$ , and the 70% kerosene ILRs, for which the mean PPMC coefficient is  $0.663 \pm 0.393$ . However, one replicate of each of these ILRs does not show any characteristic compounds of the liquid but instead, resembles the chromatogram of the burned carpet alone. When these replicates are excluded from the pair-wise comparison, PPMC coefficients indicate strong correlation among replicates of 90% evaporated gasoline ILRs ( $0.896 \pm 0.084$ ) and among replicates of the 70% evaporated kerosene ILRs ( $0.938 \pm 0.050$ ).

Mean PPMC coefficients for all gasoline ILRs indicate moderate correlation to the corresponding standard (Table 2), due to the loss of volatile compounds as a result of burning, as well as the presence of interferences (styrene, acetophenone, and the C<sub>15</sub> branched

**Table 2**

Comparison of mean Pearson product moment correlation (PPMC) coefficients  $\pm$  one standard deviation for replicates of the simulated ignitable liquid residues extracted from burned carpet correlated to replicates of the neat gasoline and neat kerosene liquid standards ( $n = 225$ ).

Mean PPMC coefficient $\pm$ standard deviation			
Ignitable liquid residue	Corresponding standard	Neat gasoline standard	Neat kerosene standard
Gasoline			
Neat	$0.640 \pm 0.053$	$0.640 \pm 0.053$	$0.551 \pm 0.063$
10% evaporated	$0.625 \pm 0.045$	$0.633 \pm 0.049$	$0.506 \pm 0.057$
90% evaporated <sup>a</sup>	$0.678 \pm 0.085$	$0.334 \pm 0.038$	$0.506 \pm 0.024$
Kerosene			
Neat	$0.803 \pm 0.085$	$0.090 \pm 0.057$	$0.803 \pm 0.085$
10% evaporated	$0.828 \pm 0.045$	$0.110 \pm 0.110$	$0.807 \pm 0.044$
70% evaporated <sup>a</sup>	$0.911 \pm 0.051$	$0.021 \pm 0.054$	$0.507 \pm 0.034$

<sup>a</sup> PPMC coefficients calculated excluding extract that contained no ignitable liquid ( $n = 180$ ).

alkanes) from the carpet matrix. Although benzaldehyde is also present only in the extracts, this compound co-elutes with *m*-ethyltoluene, which, as a compound in gasoline, is present in both the ILRs and the standards. Hence, the presence of benzaldehyde does not adversely affect the calculated coefficients.

For kerosene, mean PPMC coefficients indicate strong correlation between each simulated ILR and the corresponding standard (Table 2). Kerosene contains fewer volatile compounds and the matrix interferences contribute less to the chromatogram than for gasoline. Overall, kerosene is less affected by the burning process and the presence of matrix interferences, resulting in stronger correlations than those observed for gasoline.

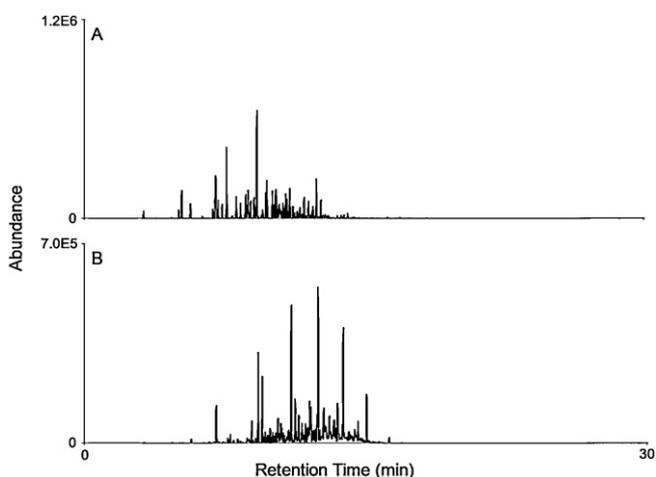
Mean PPMC coefficients were also calculated between each ILR and the neat gasoline and neat kerosene standards (Table 2). The gasoline-containing ILRs are moderately correlated to both neat standards. However, the higher coefficient indicates greater similarity of these ILRs to the neat gasoline, rather than to the neat kerosene, standard. The exception to this is the 90% evaporated gasoline ILR, which is only weakly correlated to the neat gasoline standard. The lower correlation is due to the chemical differences at this evaporation level, compared to the neat standard, as described previously. While successful association of the 90% evaporated gasoline ILR to the neat standard is not possible, association to the corresponding evaporated standard is, thus highlighting the value of including evaporated standards in reference collections.

The gasoline-containing ILRs are moderately correlated to the neat kerosene standard while the kerosene-containing ILRs are strongly correlated. The exception to this is the moderate correlation observed between the 70% evaporated kerosene ILR and the neat kerosene standard. This lower correlation (moderate rather than strong) is due to the evaporative loss of the earlier eluting aromatic compounds and normal alkanes in the ILR.

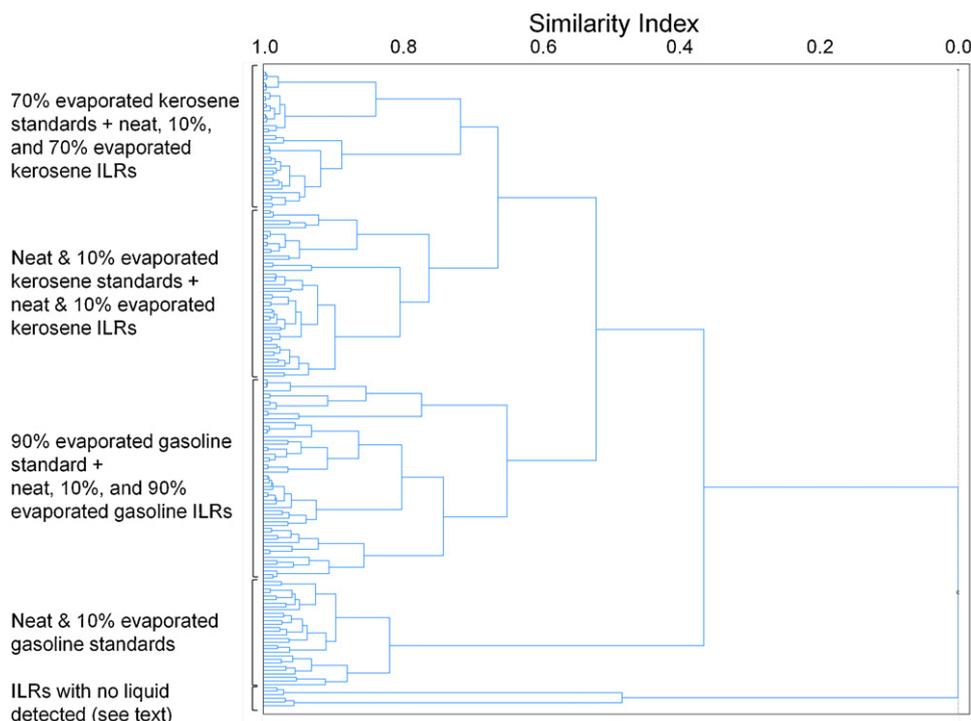
The PPMC coefficients provide a numerical assessment of the similarity between pairs of samples. However, coefficients are adversely affected by the matrix interferences since the presence of compounds in one chromatogram but not the other lowers the coefficient. Despite this, it is still possible to associate each ILR according to liquid type based on PPMC coefficients, although association to a specific evaporation level is not possible in all cases.

### 3.7. Association of simulated ILRs to liquid standards using HCA

The dendrogram for cluster analysis based on the chromatograms of the liquid standards and the simulated ILRs is shown in Fig. 8. The two ILRs for which no ignitable liquid was detected (90% evaporated gasoline and 70% evaporated kerosene) show some



**Fig. 7.** Exemplar total ion chromatograms of simulated ignitable liquid residues containing (A) neat gasoline and (B) neat kerosene.



**Fig. 8.** Dendrogram generated for gasoline and kerosene standards and extracts from burned carpet using hierarchical cluster analysis, with Euclidean distance measurement and complete linkage method.

similarity to one another (similarity index = 0.48), but no similarity (similarity index = 0) to the remainder of the standards and ILRs. All gasoline ILRs are similar to the 90% evaporated gasoline standard, forming a single cluster with a similarity index of 0.65. For the neat and 10% evaporated gasoline ILRs, loss of the  $C_2$ - and  $C_3$ -alkylbenzenes due to burning resulted in these extracts being more similar (similarity index = 0.74) to the 90% evaporated gasoline standard than to their corresponding standards. However, for the 90% evaporated gasoline ILRs, additional evaporation during burning resulted in these extracts being less similar to the corresponding 90% evaporated standard (similarity index = 0.65).

All kerosene standards and simulated ILRs are clustered with a similarity index of 0.66. Two neat kerosene and four 10% evaporated kerosene ILRs are clustered with the neat and 10% evaporated standards at a similarity index of 0.76. The 70% evaporated standards and ILRs form a cluster with a similarity index of 0.72, but this cluster also includes the remaining neat kerosene and 10% evaporated kerosene ILRs. These particular ILRs contain lower abundances of the  $C_{11}$ – $C_{15}$  normal alkanes, compared to the corresponding neat and 10% evaporated standards. As a result, the ILRs are more similar to the most evaporated standard and, hence, are clustered with the 70% evaporated kerosene standard.

Using HCA, it is possible to distinguish the ILRs according to liquid type but not to a specific evaporation level. Due to evaporative losses and the effects of burning, the ILRs are generally clustered with the most evaporated standard of the corresponding liquid type. Thus, results from HCA also highlight the importance of including evaporated standards in any reference collection used for comparison.

### 3.8. Association of simulated ILRs to liquid standards using PCA

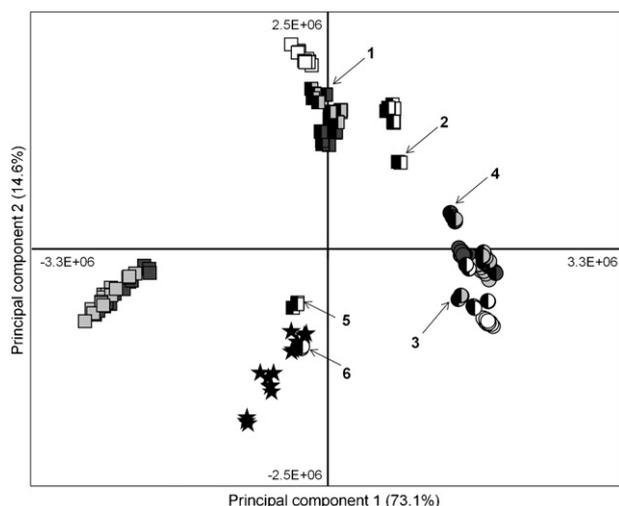
Scores calculated for the simulated ILRs were projected onto the PCA scores plot generated for the liquid standards, as shown in Fig. 9. Since the scores plot was initially generated using just the

liquid standards (Fig. 4), only those compounds present in the standards will contribute to the variance described by the eigenvectors. Consequently, matrix interference compounds will not affect positioning of the ILRs on the scores plot unless these interferences co-elute with compounds in the liquid standards. Hence, when applied in this manner, PCA acts as a filter to minimize effects from matrix interferences.

All gasoline-containing ILRs are closely positioned to the 90% evaporated gasoline standard. On PC1, the neat and 10% evaporated gasoline ILRs have similar scores to the 90% gasoline standard. In these ILRs, the more volatile toluene and  $C_2$ -alkylbenzenes are lost, whereas the  $C_3$ -alkylbenzenes and  $C_4$ -alkylbenzenes become more concentrated, during the burning process. This loss and concentration of compounds essentially mimics the evaporative losses observed in the 90% evaporated gasoline standard. Thus, the chemical similarities between the ILRs and the 90% evaporated gasoline standard results in their similar scores on PC1. In contrast, there is greater difference in positioning of the ILRs and standards on PC2. This is due to the additional contribution of the  $C_4$ -alkylbenzenes, which are weighted positively on PC2 (Fig. 5B). These compounds are present in lower abundance in the neat and 10% evaporated ILRs compared to the 90% gasoline standard. The lower abundance results in a more negative score for the ILRs on PC2, compared to the 90% evaporated standard.

The 90% evaporated gasoline ILRs are positioned more positively on PC1 in the scores plot than the corresponding evaporated standard due to the loss of the  $C_2$ -,  $C_3$ -, and  $C_4$ -alkylbenzenes during the burning process. Since these compounds are weighted negatively on PC1 (Fig. 5A), the lower abundance results in a more positive score for the 90% evaporated ILRs. The  $C_3$ - and  $C_4$ -alkylbenzenes are weighted positively on PC2 (Fig. 5B) and the lower abundance of these compounds results in the 90% evaporated gasoline ILRs being positioned less positively on PC2 in the scores plot than the corresponding standard.

Spread is apparent among the gasoline ILRs compared to the standards. For example, replicates of one ILR containing neat



**Fig. 9.** Scores plot of principal component 1 versus principal component 2 for neat and evaporated gasoline and kerosene standards, with scores projected for extracts from the burned carpet matrix. Each standard is denoted as follows: neat gasoline (■), 10% evaporated gasoline (□), 90% evaporated gasoline (□), neat kerosene (●), 10% evaporated kerosene (○), 70% evaporated kerosene (○), burned carpet with no ignitable liquid added (★). Extracts from the burned carpet samples are indicated by half fill.

gasoline (labeled 1 in Fig. 9) are positioned more positively on PC2 compared to the other neat gasoline ILRs. This is primarily due to a lower abundance of the internal standard in this particular ILR, which may be a result of inadvertently using a lower volume of dichloromethane during elution of the activated carbon strip. Since the internal standard is weighted negatively on PC2 (Fig. 5B), the lower abundance results in a less negative (*i.e.*, more positive) position for replicates of this ILR on PC2.

Spread is also apparent among replicates of the 90% evaporated gasoline ILRs, particularly in PC2, with replicates of one ILR (labeled 2 in Fig. 9) being positioned less positively on PC2 than replicates of the other ILRs. This difference in positioning is due to the lower abundance of the C<sub>2</sub>-, C<sub>3</sub>-, and C<sub>4</sub>-alkylbenzenes in this extract compared to the others.

Simulated ILRs containing kerosene are generally positioned very closely to the corresponding kerosene standard in both PC1 and PC2. However, spread is again apparent among replicates. For example, replicates of one ILR containing 10% evaporated kerosene (labeled 3 in Fig. 9) are positioned more negatively on PC2 in the scores plot than the other four ILRs. This positioning is due to the higher abundance of the internal standard in this particular ILR. Since the internal standard is weighted negatively on PC2, the increased abundance results in a more negative positioning on this PC in the scores plot.

When carpet spiked with neat kerosene is burned, the loss of C<sub>10</sub> mimics the evaporative loss observed in the ignitable liquid standards. Therefore, ILRs containing neat kerosene are expected to be more closely associated with the 10% evaporated kerosene liquid standard than with the neat kerosene standard. While this is the case for two of the five neat kerosene ILRs, the remaining three are positioned more positively on PC2 in the scores plot (labeled 4 in Fig. 9). When the chromatograms are compared, these three ILRs have a significant reduction in abundance of the internal standard peak, as well as the C<sub>10</sub>–C<sub>16</sub> normal alkanes. Since the internal standard and the normal alkanes are weighted negatively on PC2 (Fig. 5B), the lower abundance of these compounds in these three ILRs results in a less negative (*i.e.*, more positive) score on this PC than the other two extracts.

Styrene, which is present as a matrix interference, also contributes to the more positive positioning of these three neat

kerosene ILRs on PC2. Although styrene is not present in the liquid standards, this compound co-elutes with *o*-xylene, which is in gasoline. Since *o*-xylene is weighted negatively on PC2 (Fig. 5B), styrene has a negative contribution to PC2. As a result, the lower abundance of styrene in these three ILRs results in a less negative (*i.e.*, more positive) positioning on PC2 in the scores plot. It should be noted that the ILRs also contain benzaldehyde as a matrix interference. Since benzaldehyde elutes with *m*-ethyltoluene, which is present in gasoline, this compound will also contribute to positioning of the ILRs on the scores plot. However, the abundance of benzaldehyde is reproducible in all replicates of the five ILRs containing neat kerosene and consequently, benzaldehyde does not contribute to the differences in positioning on PC2 observed for these ILRs.

Replicates of one ILR containing 90% evaporated gasoline and one ILR containing 70% evaporated kerosene (labeled 5 and 6, respectively, in Fig. 9) are positioned negatively on both PC1 and PC2 and are not positioned closely to any liquid standard. The chromatograms of these replicates appear very similar to the chromatogram of the burned carpet only, indicating that no ignitable liquid is detected in either replicate, as discussed previously. Scores were calculated for the burned carpet alone and were projected onto the scores plot. The simulated ILRs containing 90% evaporated gasoline and those containing 70% evaporated kerosene are closely associated to the burned carpet, as would be expected based on visual assessment of the corresponding chromatograms.

Thus, the simulated ILRs are generally associated to a liquid of the same type but as before, cannot be associated to a specific evaporation level. Using PCA in this manner, the contribution of the matrix interferences is essentially eliminated, offering an advantage over PPMC coefficients and HCA. Shifts in positioning of the ILRs compared to the standards in the scores plot are, therefore, due to differences in chemical composition as a result of the evaporation and burning processes, as well as differences in abundance of major compounds.

#### 4. Conclusion

With increasing demand for statistical evaluation of evidence, multivariate statistical procedures are likely to become more commonplace in forensic analyses. The potential for three such procedures to associate ignitable liquid residues to liquid standards, even in the presence of evaporation and matrix interferences, was demonstrated in this proof-of-concept work.

For all three statistical procedures, association of the extracts according to liquid type was generally possible, albeit not necessarily to the specific level of evaporation. Despite generating similar results, the procedures differ inherently in the mode of operation, as well as the manner in which results are displayed.

Pearson product moment correlation coefficients and HCA are both based on assessing similarity among samples. A PPMC coefficient is a single number that demonstrates the correlation between pairs of samples, allowing simpler comparison of large data sets. However, for the pair-wise comparison of *n* samples, *n*<sup>2</sup> PPMC coefficients are generated, making comparisons more time consuming. In contrast, HCA offers the advantage of comparing all samples simultaneously. The resulting similarities among the data set are displayed as a dendrogram, giving a graphical representation of the results. Once these statistical procedures are fully validated and routinely implemented in forensic laboratories, the HCA dendrogram may prove more useful for presentation in court, rather than PPMC coefficients. However, as demonstrated in this research, both procedures are adversely affected by the presence of matrix interferences.

Principal components analysis also offers graphical demonstration of the similarities and differences among samples in the form of the scores plot. In this research, PCA was firstly performed on the liquid standards alone and scores for the ILRs were then calculated and projected onto the plot. As a result, only matrix interferences that elute at the same retention time as compounds in the standards affect the positioning of the ILRs on the scores plot. That is, PCA essentially serves as a filter to eliminate the matrix interferences, such that positioning of the ILRs is most affected by liquid type.

While proof-of-concept in nature, this research demonstrates that further studies in this area are warranted. A larger, perhaps more diverse, data set should be considered such that the significance of the results can be more fully demonstrated in a forensic context. In this research, all data points in the chromatogram were considered to avoid subjectivity associated in the selection of peaks or sections of the chromatogram for data analysis procedures. In future work, the mass spectral data should also be considered, potentially using commercially available software programs to identify the most variable mass-to-charge ratios for subsequent data analysis. Additional statistical procedures should also be investigated to assess association of the extract to liquid standards despite evaporation and matrix interferences, as well as thermal degradation and pyrolysis products from both the liquid and the matrix.

#### Acknowledgements

The Midwest Forensics Resource Center is acknowledged for financial support of this project, under Prime Contract No. DE-AC02-07CH11358. Mr. Troy Ernst (Michigan State Police Forensic Science Division) is also acknowledged for insight regarding practical considerations in a forensic laboratory. Mr. Dayle Frame (Analytical Sciences) is also gratefully acknowledged for use of the automatic liquid sampler for the GC–MS system.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.forsciint.2012.06.010>.

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