Application of Multivariate Statistical Procedures in Fire Debris Analysis: Investigating Matrix Interference Effects and Weathering of Ignitable Liquids on Association of Ignitable Liquid Residues to Neat Ignitable Liquids

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Project Description

Further development of an objective methodology to associate ignitable liquid residues (ILRs) in fire debris to the neat liquid is proposed. A series of studies will be conducted to assess the effect of matrix interferences and weathering on the association of ILRs to the neat liquid. Principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients will initially be used for objective association. The potential of a soft independent modeling of class analogy (SIMCA) approach to classify an ILR to an ignitable liquid class, with statistical confidence, will then be investigated to enhance the objectivity of the proposed method.

Project Objectives

The research goals for this preliminary research are defined as follows:

1. Investigate increased matrix interference effects from three household matrices currently in our 'in-house' reference collection,
2. Investigate the effect of increased matrix interference effects on the association of evaporated liquids to neat liquids using PCA and PPMC coefficients,
3. Investigate the association of simulated ILRs to the corresponding neat liquid using PCA and PPMC coefficients, and
4. Investigate a SIMCA approach for the classification of a simulated ILR to an ignitable liquid class.

Project Accomplishments

1. Effect of evaporation of three ignitable liquids (gasoline, kerosene, and lighter fluid) on association of the liquid to the corresponding standard investigated.
2. Inherent matrix interferences identified in three household matrices: nylon carpet, high-density polyethylene (HDPE), and carpet padding.
3. Matrix interferences identified in the above three matrices after burning.
4. Effect of inherent matrix interferences on association of the neat and evaporated ignitable liquids to the corresponding liquid standard investigated, using principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients.
5. Effect of evaporation, matrix interferences, and thermal degradation on association of the neat and evaporated ignitable liquids to the corresponding liquid standard investigated, using PCA and PPMC coefficients.

Summary of Results

Detailed procedures and discussion of results were included in each of the four quarterly reports submitted throughout the duration of this project. The following is only intended as a brief summary of the results obtained.

Association of Evaporated Liquids to Corresponding Liquid Standard

Gasoline, kerosene, and lighter fluid were purchased locally and evaporated under a stream of purified air. Gasoline and lighter fluid were evaporated to 10% and 90% (v/v) while kerosene was evaporated to 10% and 70% (v/v). The neat and evaporated liquids

were diluted 1:100 (v/v) in dichloromethane that contained 0.03 M nitrobenzene as an internal standard. The diluted liquids were spiked (20 μL) onto a Kimwipe™ and placed in a nylon bag with an activated carbon strip. The bag was sealed using general purpose masking tape and extracted in an oven at 80 °C for four hours.

Following extraction, the carbon strip was eluted with 200 μL of dichloromethane that was then analyzed by gas chromatography-mass spectrometry (please see Quarterly Reports for details). All extracts were analyzed in triplicate and the resulting total ion chromatograms (TICs) were subjected to various pretreatment procedures prior to data analysis. Firstly, the caprolactam peak in each TIC, which originates from the nylon bags, was subtracted using ChemStation software. Then, TICs were smoothed, using the appropriate function available in the ChemStation software.

Total ion chromatograms were retention time aligned to a concensus target using a correlation optimized warping algorithm. The concensus target was prepared by combining aliquots of each of the three neat liquids in dichloromethane. Finally, TICs were normalized in a two-step process. The first step involved normalization of each TIC to the internal standard. The second step involved total area normalization of either each set of replicates at a given evaporation level or each set of individual replicates (please see Quarterly Reports for specific details).

Principal components analysis was then performed on the pretreated TICs of the neat and evaporated liquid standards. The eigenvectors and eigenvalues were then plotted to generate scores and loadings plots that were used to assess the association of the evaporated liquids to the corresponding neat liquid. Pearson product moment correlation coefficients were also calculated for every pair-wise comparison of TICs. Coefficients

calculated between pairs of replicates were used to assess precision in the extraction and analysis procedures. Coefficients were also calculated between the evaporated and neat standards to assess the similarity between them.

Throughout the course of the research, multiple sets of liquid standards were prepared and analyzed. One example of a typical scores plot for the standards is shown in Figure 1, in which the first two principal components account for 75.94% of the total variance among the liquid standards. Replicates of each liquid standard are grouped closely, with sufficient distinction among the different liquid types. Gasoline is positioned positively on the first principal component (PC1), while kerosene and lighter fluid are positioned negatively. However, the latter two liquids can be distinguished on the second principal component (PC2) since kerosene is positioned negatively and lighter fluid is positioned positively on this PC.

The positioning of the standards can be explained with reference to the loadings plots (Figure 2). Toluene, C_2-, C_3-, and C_4-alkylbenzenes, along with the internal standard are weighted positively on PC1 (Figure 2A), while the C_9-C_{11} and C_{13}-C_{16} normal alkanes are weighted negatively. On PC2 (Figure 2B), 1,3,5-trimethylbenzene (a C_3-alkylbenzene) and C_9-C_{11} are weighted positively, while toluene and C_{12}-C_{16} are weighted negatively.

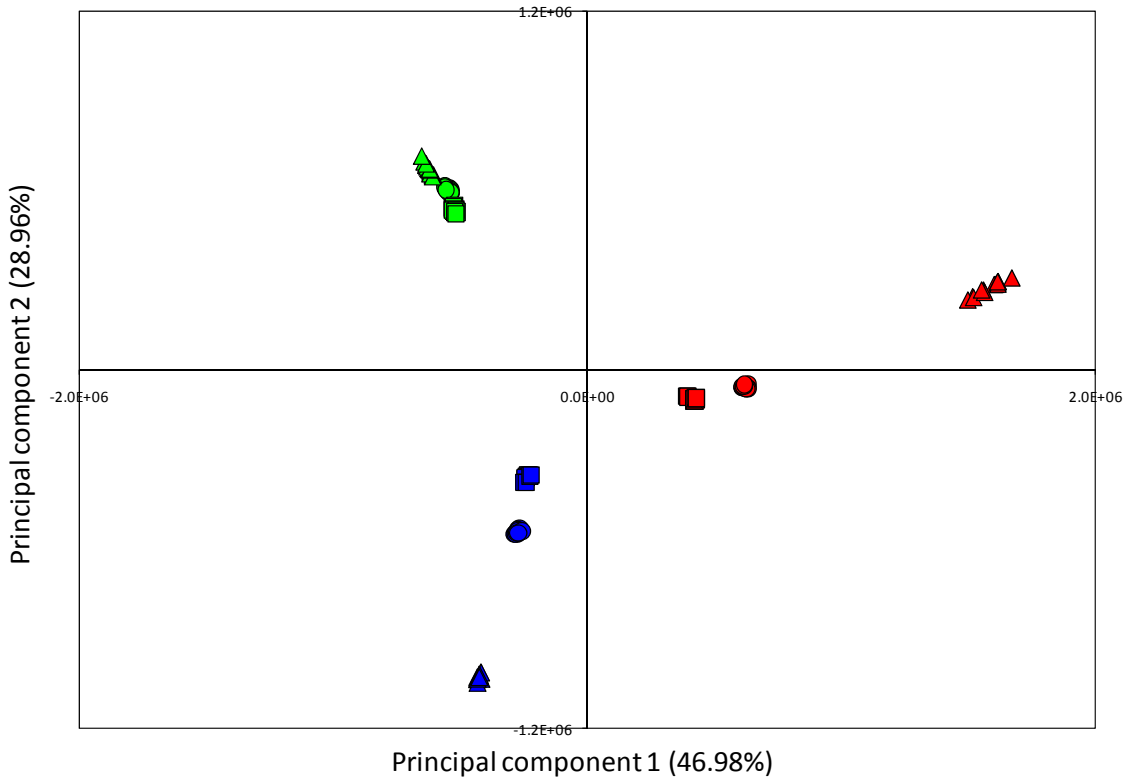

Figure 1. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards used in the carpet padding data sets. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

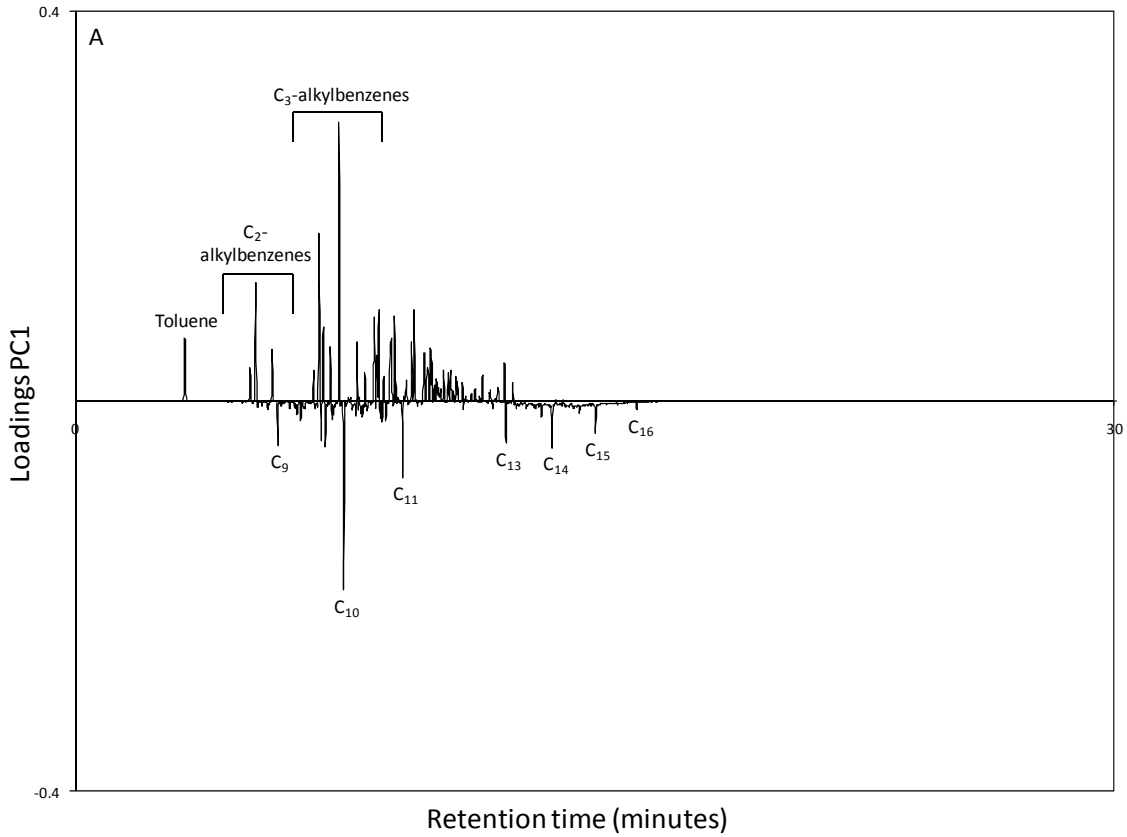

Figure 2. Loadings plot for (A) principal component 1 and (B) principal component 2 based on the total ion chromatograms for the neat and evaporated liquid standards used in the data set containing the carpet padding matrix.

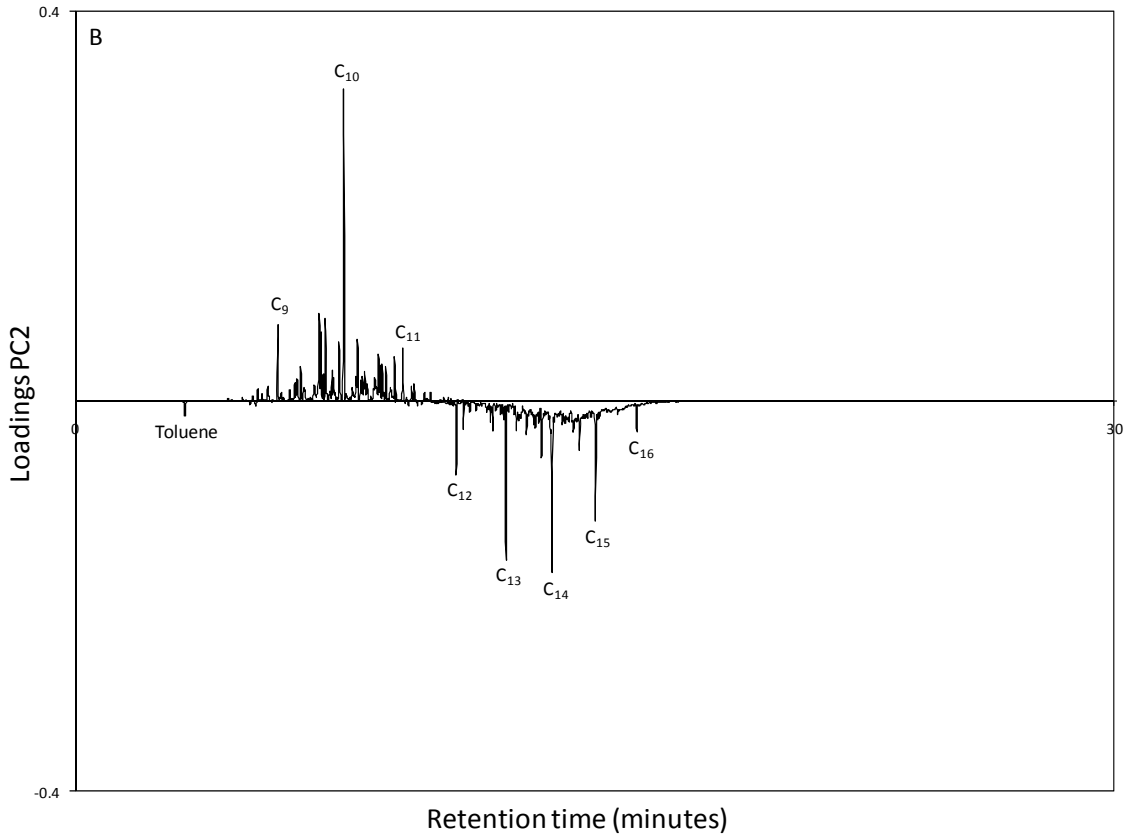

Figure 2 contd. Loadings plot for (A) principal component 1 and (B) principal component 2 based on the total ion chromatograms for the neat and evaporated liquid standards used in the data set containing the carpet padding matrix.

In the scores plot (Figure 1), the gasoline standards are positioned positively on PC1 due to the positive weighting of the characteristic gasoline compounds on this PC. Similarly, the lighter fluid and kerosene standards are positioned negatively on PC1 in the scores plot since the normal alkanes that are characteristic of these liquids are weighted negatively on this PC.

On PC2 in the scores plot, the neat and 10% evaporated gasoline standards are positioned negatively due to the high abundance of toluene (weighted negatively on PC2) in these standards. In contrast, the 90% evaporated gasoline standard contains no toluene and is positioned positively on PC2 in the scores plot due to the high abundance of 1,3,5-trimethylbenzene, which is weighted positively on this PC.

The kerosene standards are all positioned negatively on PC2 in the scores plot due to the negative weighting of the C_{13}-C_{16} normal alkanes on this PC. Additionally, the 70% evaporated kerosene standard is weighted more negatively on PC2 due to the greater abundance of C_{13} and C_{14} in this standard compared to the neat and 10% evaporated standards. These two normal alkanes are weighted most negatively on PC2, resulting in the more negative positioning of the 70% evaporated standard. The lighter fluid standards are all positioned positively on PC2 in the scores plot due to the positive weighting of the characteristic lighter fluid compounds (C_9, C_{10}, and C_{11}) on PC2.

Mean PPMC coefficients and the range of coefficients for replicates of the liquid standards are shown in Table 1. Theoretically, replicates are expected to have a coefficient equal to 1.00; however, in this case, replicates (n=3) of different extracts (n=5) of each liquid are included in the calculation. Hence, the slightly lower coefficients account for variability not only in the instrumental analysis, but also in the extraction

procedure. Nonetheless, the mean coefficients demonstrate strong correlation among replicates of each liquid, indicating acceptable precision in the extraction and analysis procedures.

Table 1. Mean and range of Pearson product moment correlation coefficients for replicates (n=105) of each liquid standard.

Liquid standard	Mean PPMC coefficient ± standard deviation	Range of PPMC coefficients
Neat gasoline	0.988 ± 0.014	1.000 - 0.955
10% evaporated gasoline	0.996 ± 0.003	1.000 - 0.989
90% evaporated gasoline	0.997 ± 0.001	1.000 - 0.997
Neat kerosene	0.996 ± 0.003	1.000 - 0.986
10% evaporated kerosene	0.992 ± 0.006	0.999 - 0.978
70% evaporated kerosene	0.994 ± 0.005	1.000 - 0.983
Neat lighter fluid	0.995 ± 0.006	1.000 - 0.974
10% evaporated lighter fluid	0.997 ± 0.003	1.000 - 0.988
90% evaporated lighter fluid	0.989 ± 0.011	1.000 - 0.965

Investigation of matrix interferences in nylon carpet, HDPE, and carpet padding

Samples of each of the three matrices were placed in nylon bags that also contained an activated carbon strip. Samples were extracted at 80 °C for four hours, then eluted with dichloromethane, as described previously. In addition, samples of each matrix were also burned using a propane blowtorch for burn times of 10, 20, 30, 60, and 120 s. The burned samples were also extracted in a similar manner. All extracts were analyzed in triplicate by GC-MS and compounds in each extract were identified through comparison of mass spectral data with the National Institute of Standards and Technology (NIST) Mass Spectral Search Program.

Exemplar chromatograms of each unburned and burned matrix are shown in Figures 3-5. For carpet, the inherent interferences are C_9-C_{12} branched alkanes (Figure 3A) and, as burning progresses (Figure 3B), styrene, benzaldehyde, and acetophenone are present at greater abundance. For HDPE, the unburned matrix is dominated by the alkenes, dodecene, tetradecene, and hexadecene, with decene, dodecane, and tetradecane also present, albeit at lower abundance (Figure 4A). With burning, the characteristic bell-shaped triplet of peaks expected as polyethylene thermally degrades becomes apparent. During degradation, HDPE breaks down *via* a random scission process, which results in the formation of an alkadiene, an alkene, and an alkane for each carbon number. After 60 seconds of burning, the alkadiene, alkene, and alkane for C_8-C_{16} are readily visible (Figure 4B).

Unburned carpet padding contains numerous inherent interferences, including phenol, 1-octanol, 2-ethyl-hexanoic acid, a substituted phenols, and butylated hydroxytoluene, as shown in Figure 5A. After burning for 30 s, additional interferences

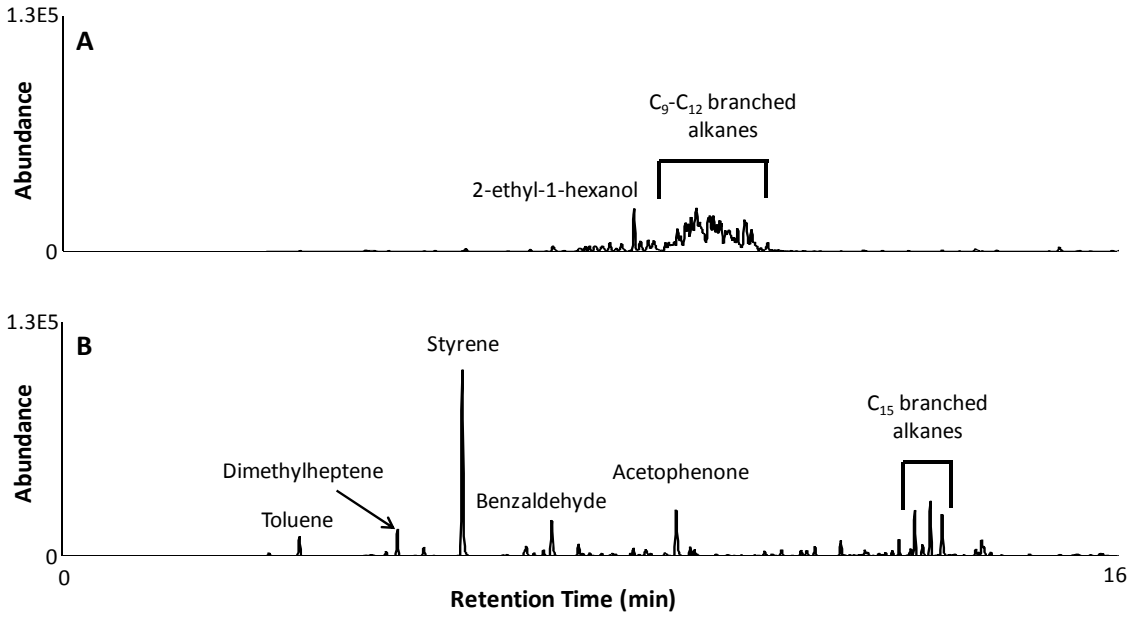

Figure 3. Representative total ion chromatogram of nylon carpet after burning for (A) 0 seconds and (B) 60 seconds.

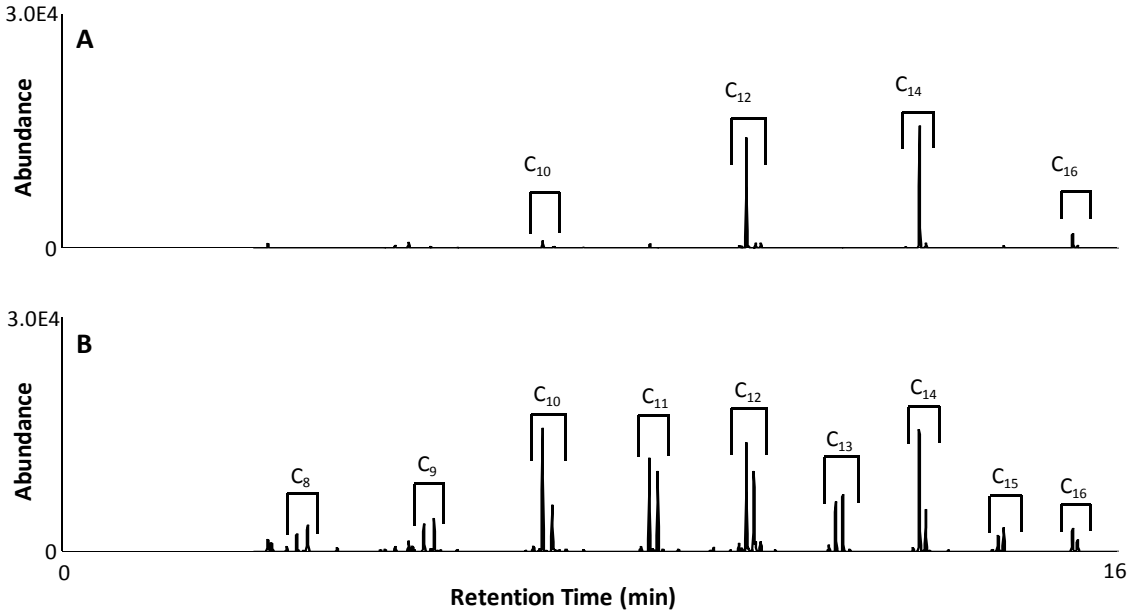

Figure 4. Representative total ion chromatogram of high density polyethylene after burning for (A) 0 seconds and (B) 60 seconds.

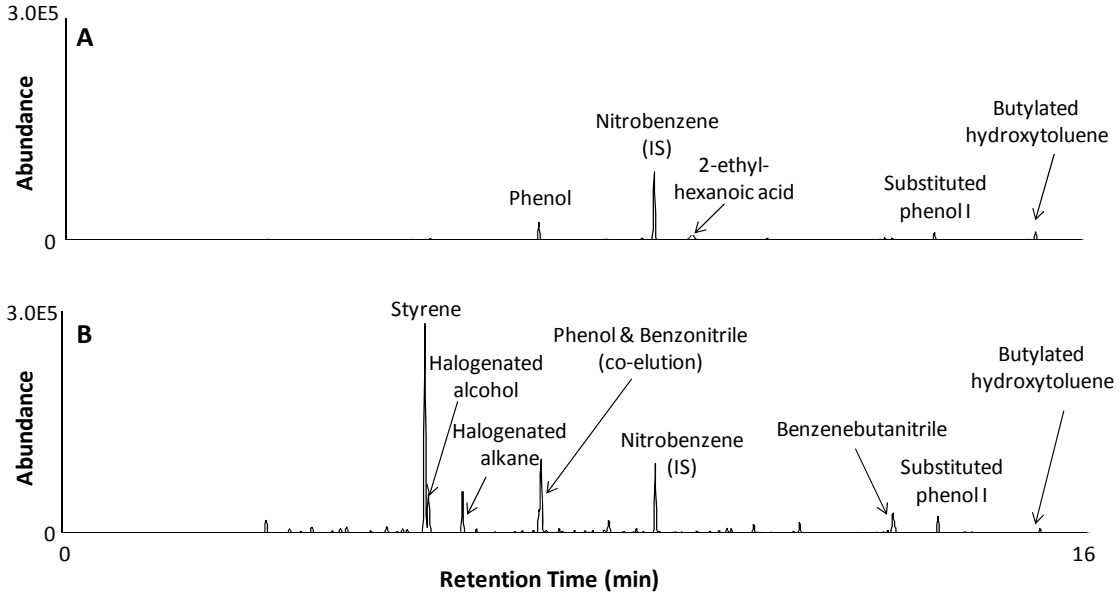

Figure 5. Representative total ion chromatogram of carpet padding after burning for (A) 0 seconds and (B) 30 seconds.

including styrene, a halogenated alcohol, a halogenated alkane, benzonitrile, and benzenebutanitrile are also apparent (Figure 5B).

In each case, the presence of matrix interferences poses problems for identification of gasoline, kerosene, and lighter fluid in the TIC. The presence of these interferences not only introduces additional compounds into the TIC, but can also disrupt the expected ratios of the characteristic compounds in the ignitable liquids.

Effect of matrix interferences on association of extracts to corresponding liquid standard using PCA

Each matrix was burned for a specified time that was previously determined to generate matrix interferences at sufficiently high abundance. For carpet and HDPE, the burn time was 60 s, while for carpet padding, the burn time was 25 s. Samples of the burned matrices were then spiked with each of the ignitable liquid standards (both neat and evaporated), then extracted and analyzed following procedures described previously. The resulting TICs were combined with the TICs of the appropriate liquid standards and then subjected to the data pretreatment procedures (*i.e.*, subtraction of the caprolactam peak, smoothing, retention time alignment, and normalization).

Principal component analysis was performed on the TICs of only the liquid standards, and scores and loadings plots were generated from the calculated eigenvectors and eigenvalues. Data for the extracts from the burned matrices were mean-centered to the liquid standards. Each mean-centered extract was multiplied by the eigenvector for PC1 and the product was summed to generate the score for that extract on PC1. A similar procedure was conducted multiplying the mean-centered extract by the eigenvector for

PC2 to generate the score for the extract on PC2. The calculated scores were then projected onto the scores plot to assess association of the liquids extracted from the burned matrices to the corresponding liquid standards. By performing PCA in this manner, only compounds present in the liquid standards, or compounds that elute at the same retention time as those in the standards, affect positioning of the extracts on the scores plot. As such, matrix interferences, which are only present in the extracts, are essentially filtered out, and do not affect positioning.

Burned Carpet

The scores plot with scores projected for the liquids extracted from burned carpet is shown in Figure 6. The first two PCs cumulatively account for 76.46% of the variance in the data set. Overall, extracts are positioned closely to the corresponding standard in the scores plot although there are some slight discrepancies. The neat gasoline extracts are positioned slightly more negatively on PC1 than the corresponding standard. Comparing the TICs of the neat gasoline extracts and standards, it is apparent that the internal standard is present in lower abundance in the extracts. Since the internal standard is weighted positively on PC1, the lower abundance in the extracts results in a less positive (*i.e.*, more negative) positioning on this PC in the scores plot compared to the standards. A similar argument also holds true for the more negative positioning of the 10% evaporated gasoline extracts compared to the standards on PC1 in the scores plot. The 90% evaporated gasoline extracts are positioned more positively on PC2 than the corresponding standard, due to differences in the abundance of toluene. This compound is present in greater abundance in the extracts and, since toluene is

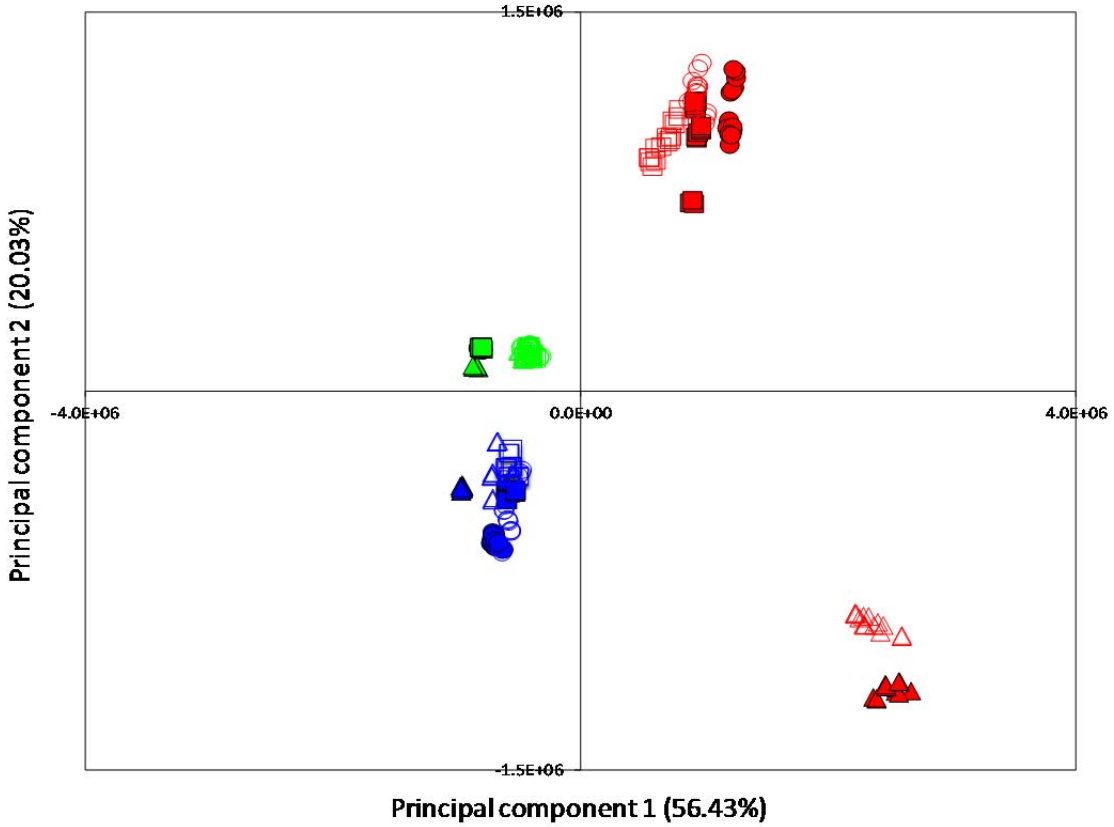

Figure 6. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the liquids extracted from burned carpet. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

weighted positively on PC2, there is a greater positive contribution for the extracts compared to the standards on this PC.

The neat and 10% evaporated kerosene extracts are positioned closely to the corresponding standards in the scores plot, while the 70% evaporated extract is more positive on PC1 than the appropriate standard. This slight shift in positioning is due to differences in the abundance of the internal standard, which is significantly more abundant in the extracts compared to the standards. And, since the internal standard is weighted positively on PC1, the greater positive contribution results in the 70% evaporated kerosene extracts being positioned more positively on this PC in the scores plot compared to the corresponding standard.

All lighter fluid extracts are positioned more positively on PC1 in the scores plot than the corresponding standards. This difference is again due to the substantially greater abundance of the internal standard in the extracts compared to the standards, as described above for the 70% evaporated kerosene extracts and standards.

Burned HDPE

A new set of liquid standards was used for the HDPE matrix, resulting in a different scores plot to that shown previously for the burned carpet data. In this case, the first two PCs cumulatively account for 85.25% of the total variance in the data set and, as before, the positioning of all liquids can be explained with reference to the appropriate loadings plots (data not shown).

When scores for liquids extracted from burned HDPE are projected onto the scores plot (Figure 7), the gasoline extracts are all positioned similarly on PC1 to

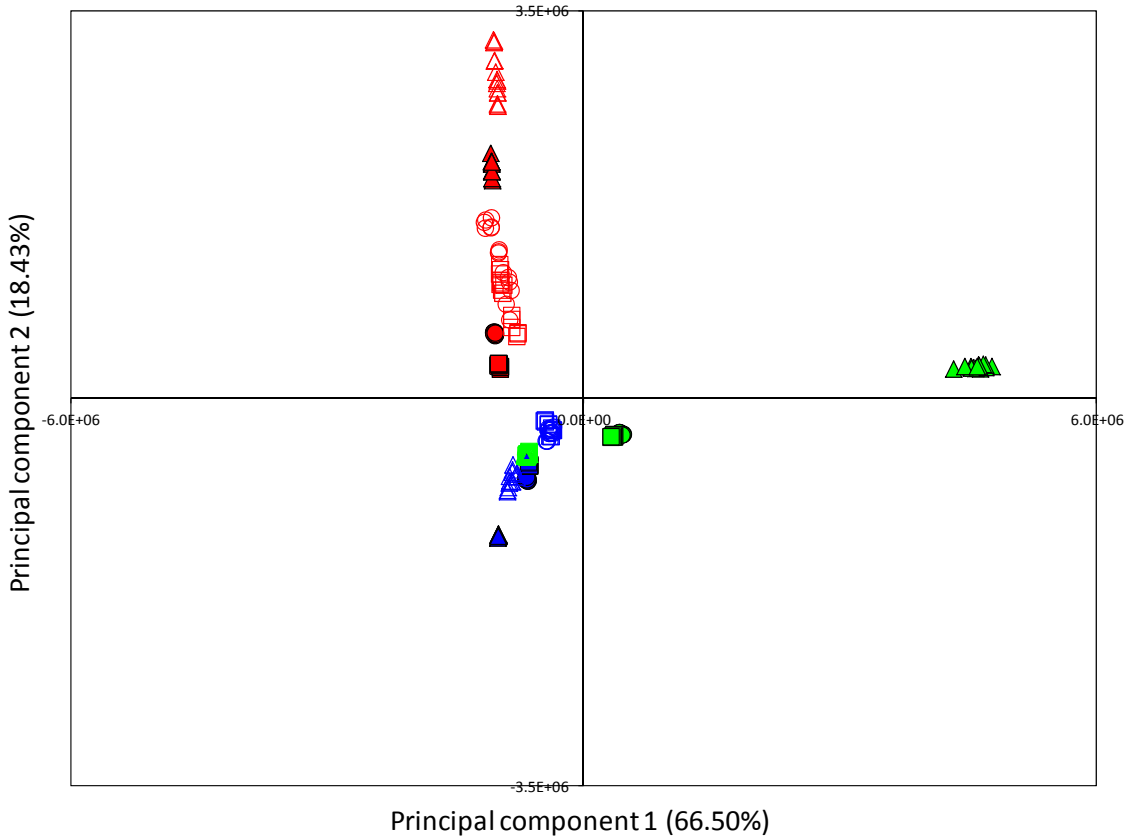

Figure 7. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the liquids extracted from burned high density polyethylene. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

the corresponding standard but are positioned more positively on PC2. The extracts containing neat and 10% evaporated gasoline have greater abundance of toluene, C_2-alkylbenzenes, C_3-alkylbenzenes, and C_4-alkylbenzenes than the standards. At the 90% evaporation level, the liquid is dominated by the C_3-alkylbenzenes and C_4-alkylbenzenes and the 90% evaporated extracts contain greater abundance of these compounds than the standards. Since the characteristic gasoline compounds are weighted positively on PC2, the higher abundance results in a more positive score for these extracts on PC2. The same compounds are not as significantly weighted on PC1 and hence, the positioning of the extracts compared to the standards is not as affected on PC1.

The kerosene extracts have similar score on PC1 to the corresponding standards, although have a more positive score on PC2. Both the neat and 10% evaporated extracts contain toluene, which is present as a contaminant in the HDPE matrix. However, since toluene is also a compound in gasoline, the presence of this particular contaminant does affect positioning of the extracts on the scores plots. In this case, toluene has a positive contribution on PC2; as a result, the additional positive contribution that is only in the extracts results in the extracts being positioned more positively on PC2 than the standards. For 70% evaporated kerosene, the extracts contain a substantially lower abundance of the C_{13}-C_{16} normal alkanes than the standard. Since these alkanes are weighted negatively on PC2, the lower abundance in the extracts results in a less negative (*i.e.*, more positive) position in the scores plot compared to the standards.

All lighter fluid extracts are positioned more negatively in the scores plot on both PCs compared to the corresponding standards. These extracts are dominated by the internal standard and contain low abundance of the C_9-C_{11} normal alkanes that are

characteristic of this lighter fluid. The extracts also contain the C_{13}-C_{16} normal alkanes as matrix interferences from the HDPE. Since these compounds are weighted negatively on both PCs, the extracts have a more negative score and are positioned closer to the kerosene standards in the scores plot.

Overall, gasoline extracts can be associated to a gasoline standard although, for neat and 10% evaporated gasoline, it is not possible to associate to one evaporation level over another. Similarly, the kerosene extracts can be associated to kerosene but again, not to the specific evaporation level. Through visual assessment of the PCA scores plot, it is not possible to associate lighter fluid to the corresponding standard; instead, lighter fluid is associated with kerosene. However, this positioning is mainly due to the presence of the normal alkane matrix interferences, which are characteristic compounds in kerosene.

Burned Carpet Padding

The scores plot with the extracts from the burned carpet padding projected is shown in Figure 8. For gasoline, the neat and 10% evaporated extracts are positioned more positively on both PC1 and PC2 than the corresponding standards. The extracts contain greater abundance of toluene, C_2-alkylbenzenes, and C_3-alkylbenzenes than the standards and, since these compounds are weighted positively on PC1, the extracts are positioned more positively on this PC in the scores plot. The gasoline compounds contributing to the variance in PC2 are toluene and 1,3,5-trimethylbenzene. The contribution of 1,3,5-trimethylbenzene in the loadings plot is greater than that of toluene and, since 1,3,5-trimethylbenzene is weighted positively, the extracts are positioned more positively on PC2 than the standards.

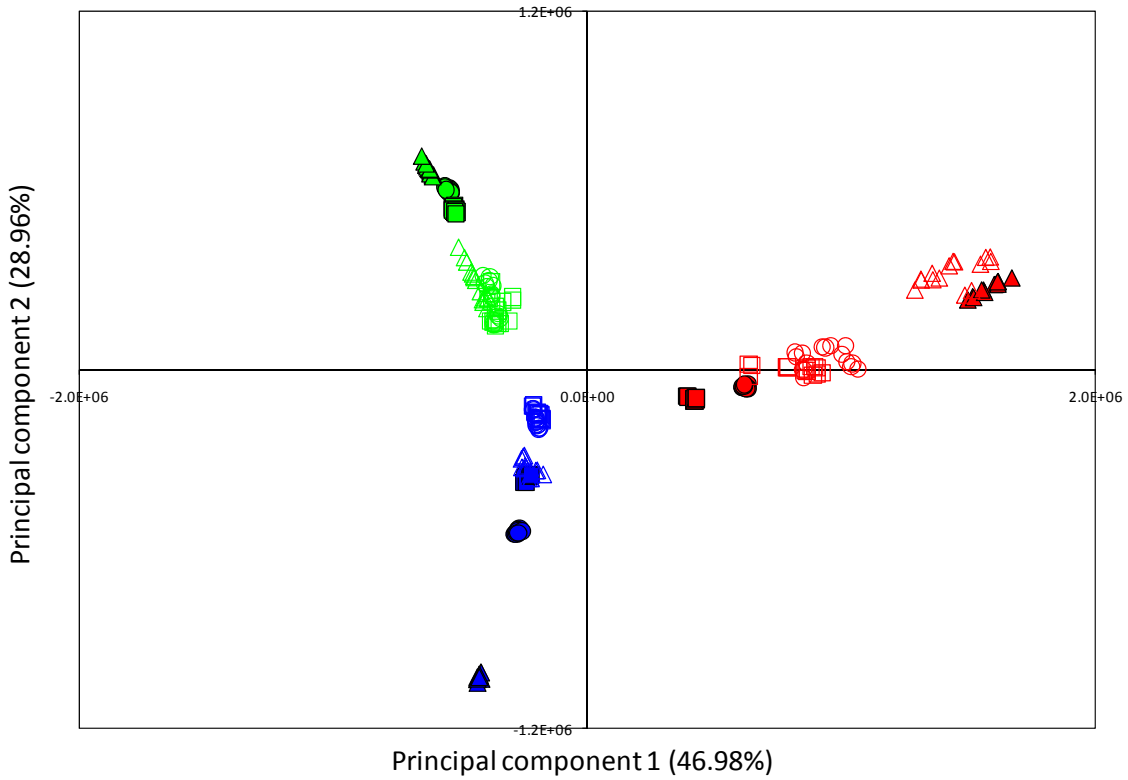

Figure 8. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the liquids extracted from burned carpet padding. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

The 90% evaporated gasoline extracts are positioned very closely to the corresponding standard in both PC1 and PC2. Neither extract nor standard contain toluene and both contain similar abundance of the C_2- and C_3-alkylbenzenes, resulting in the close positioning in the scores plot.

The kerosene extracts are also positioned similarly on PC1 in the scores plot, but more positively on PC2, than the corresponding standards. In this case, the extracts all contain lower abundance of the characteristic normal alkanes compared to the standards. Since these alkanes are weighted negatively, the lower abundance results in a less negative (*i.e.*, more positive) positioning in the scores plot. These normal alkanes have greater contribution to PC2 than to PC1 and hence, positioning of the extracts is more affected on PC2 than PC1.

The lighter fluid extracts are positioned similarly on PC1 in the scores plot, but more negatively on PC2, than the corresponding standards. For all three extracts, the abundance of C_9, C_{10}, and C_{11} is substantially less than that in the standard. Since these three compounds are all weighted positively on PC2, the lower abundance results in a less positive (*i.e.*, more negative) positioning of the extracts in the scores plot. And, since these compounds have greater contribution to PC2 than to PC1, positioning of the extracts is more affected on PC2.

In summary, it is possible to associate each of the liquids extracted from the burned carpet padding to the appropriate liquid standard, based on visual assessment of the scores plot. However, and as observed for previous matrices, association of the extract to the corresponding evaporation level is not possible.

Effect of matrix interferences on association of extracts to corresponding liquid standard using PPMC coefficients

Pearson product moment correlation coefficients were also calculated to assess association of each extract from each of the burned matrices to the corresponding liquid standard, as well as to the neat liquid standards.

Burned Carpet

The calculated PPMC coefficients are summarized in Table 2. For gasoline, strong correlation is observed between all extracts and the corresponding standards. Neat and 10% evaporated gasoline show strong correlation to the neat gasoline standard, while there is only moderate correlation between the 90% evaporated gasoline extract and neat gasoline standard. This lower correlation is primarily due to the significant differences in chemical composition between neat gasoline and 90% evaporated gasoline, in addition to the matrix interferences that are only present in the extracts. All gasoline extracts show only weak correlation to neat lighter fluid and neat kerosene standards, indicating that differentiation among the liquids is possible.

Strong correlation is observed for the neat and 10% evaporated kerosene extracts and the corresponding standards. However, only moderate correlation is observed between the 70% evaporated extract and corresponding standard. In the 70% evaporated kerosene standard, there is a higher abundance of compounds eluting between the normal alkanes that results in an unresolved envelope of peaks. Since a similar envelope of peaks is not observed to the same extent in the 70% evaporated kerosene extract, this difference results in lower coefficients when compared to the standard. The neat and 10%

Table 2. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from burned carpet correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from burned carpet	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.904 ± 0.027	0.283 ± 0.013	0.904 ± 0.027	0.354 ± 0.018
10% evaporated gasoline	0.901 ± 0.018	0.258 ± 0.017	0.875 ± 0.033	0.318 ± 0.022
90% evaporated gasoline	0.976 ± 0.004	0.285 ± 0.005	0.651 ± 0.016	0.371 ± 0.008
Neat kerosene	0.843 ± 0.062	0.489 ± 0.049	0.444 ± 0.048	0.843 ± 0.062
10% evaporated kerosene	0.800 ± 0.068	0.383 ± 0.034	0.361 ± 0.054	0.790 ± 0.067
70% evaporated kerosene	0.729 ± 0.073	0.290 ± 0.046	0.388 ± 0.048	0.688 ± 0.071
Neat lighter fluid	0.679 ± 0.024	0.679 ± 0.024	0.606 ± 0.067	0.766 ± 0.026
10% evaporated lighter fluid	0.680 ± 0.027	0.697 ± 0.022	0.607 ± 0.066	0.771 ± 0.024
90% evaporated lighter fluid	0.675 ± 0.030	0.712 ± 0.20	0.600 ± 0.065	0.795 ± 0.023

evaporated kerosene extracts show strong correlation (within one standard deviation) to the neat kerosene standard, while the 70% evaporated kerosene extract shows only moderate correlation to the neat standard. The lower correlation for the most evaporated liquid is due to the substantial differences in chemical composition as a result of evaporation (*i.e.*, aromatic compounds eluting before t_R 9 minutes), in addition to matrix interferences from the burned carpet. Nonetheless, all kerosene extracts are only weakly correlated to the neat lighter fluid and neat gasoline standards, allowing discrimination of the kerosene extracts from the other two liquid types.

Only moderate correlation is observed for lighter fluid extracted from the burned carpet compared to the corresponding standard. The extracts contain styrene (t_R 5.6 minutes) as a matrix interference, as well as later-eluting compounds (t_R 12.2, 12.5, 12.7, and 12.8 minutes), potentially resulting in lower correlation to the standard. Extracts of lighter fluid from the burned carpet show moderate correlation to both the neat gasoline and neat kerosene standards. Correlation to neat kerosene is slightly higher due to the presence of the normal alkanes C_{10} and C_{11} that are present in both kerosene and lighter fluid.

In summary, it is possible to associate gasoline and kerosene extracted from burned carpet to the corresponding neat standard using PPMC coefficients: for both liquids, extracts show moderate to strong correlations to the corresponding neat standard, but only weak correlation to standards of the other two liquids. Extracts of lighter fluid show moderate correlation to all three neat liquid standards such that association to the corresponding liquid is not possible based solely on PPMC coefficients. However, lighter fluid extracts and standards are positioned closely, and distinctly from gasoline

and kerosene, in the PCA scores plot, thus allowing association of the extracts to the appropriate standard when the two statistical procedures are considered together.

Burned HDPE

Calculated coefficients for the liquids extracted from the burned HDPE matrix are summarized in Table 3. When the standard deviation is taken into account, all gasoline extracts show strong correlation to the corresponding standard. Gasoline extracts have a weak correlation to the neat lighter fluid standard due to substantially different chemical composition. The neat and 10% evaporated gasoline extracts are strongly correlated to the neat gasoline standard (within one standard deviation), while the 90% evaporated gasoline extract is only moderately correlated to the same standard. This lower correlation is primarily due to the difference in chemical composition as a result of evaporation (*i.e.*, loss of toluene, one of the characteristic gasoline compounds), in addition to the presence of matrix interferences in the extract.

The gasoline extracts show weak to moderate correlation to the kerosene standard. In fact, the mean PPMC coefficients are higher for comparison to kerosene than to lighter fluid, indicating greater similarity. This is due to the nature of the matrix interferences, which are normal alkanes (C_{12}-C_{16}) that are already present in kerosene. Hence, their presence in gasoline increases the similarity of the gasoline extracts to the kerosene standard.

Kerosene extracts show only moderate correlation to the corresponding standard, which initially, seems unexpected. However, the neat and 10% evaporated kerosene

Table 3. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from burned HDPE correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from burned HDPE	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.793 ± 0.091	0.374 ± 0.022	0.793 ± 0.091	0.521 ± 0.038
10% evaporated gasoline	0.868 ± 0.040	0.349 ± 0.023	0.858 ± 0.043	0.456 ± 0.033
90% evaporated gasoline	0.910 ± 0.009	0.358 ± 0.010	0.670 ± 0.027	0.491 ± 0.012
Neat kerosene	0.753 ± 0.099	0.484 ± 0.067	0.473 ± 0.065	0.753 ± 0.099
10% evaporated kerosene	0.743 ± 0.034	0.448 ± 0.023	0.448 ± 0.041	0.777 ± 0.031
70% evaporated kerosene	0.619 ± 0.028	0.358 ± 0.029	0.397 ± 0.045	0.713 ± 0.030
Neat lighter fluid	0.576 ± 0.032	0.576 ± 0.032	0.496 ± 0.059	0.679 ± 0.037
10% evaporated lighter fluid	0.565 ± 0.037	0.571 ± 0.030	0.496 ± 0.057	0.683 ± 0.034
90% evaporated lighter fluid	0.212 ± 0.021	0.486 ± 0.049	0.431 ± 0.063	0.604 ± 0.057

extracts contain toluene as an interference from the HDPE matrix, in addition to the normal alkane interferences, resulting in the lower than expected correlation. The 70% evaporated kerosene extracts are only moderately correlated to the corresponding standard due to greater abundance of unresolved peaks that elute between the normal alkanes in the standard. This results in a higher baseline in the standard that is not present to the same extent in the extracts, thus lowering the correlation coefficient.

The kerosene extracts are weakly correlated to the neat lighter fluid and neat gasoline standards, as expected due to differences in chemical composition. The neat and 10% evaporated kerosene extracts show moderate correlation to the neat kerosene standard, primarily again due to the presence of toluene which lowers the coefficient. The 70% evaporated kerosene also shows moderate correlation to the neat standard, which is due to the significant changes in chemical composition as a result of evaporation (*i.e.*, loss of C_{10} and C_{11}).

The neat and 10% evaporated lighter fluid extracts are moderately correlated to the corresponding standards, while the 90% evaporated extract is only weakly correlated to the appropriate standard. All lighter fluid extracts are dominated by the internal standard and show few compounds from the liquid itself, primarily only C_9, C_{10}, and C_{11}. However, in the 90% evaporated extract, C_9 has been lost, lowering the coefficient even further. The extracts show moderate to weak correlation to the neat lighter fluid standard and weak correlation to the neat gasoline standard, due to differences in chemical composition. In contrast, the lighter fluid extracts show moderate correlation to the neat kerosene standard. This is due to the presence of the normal alkanes (C_{13}-C_{16}), which are

matrix interferences in the lighter fluid extracts and characteristic compounds in the kerosene standard.

Overall, the gasoline extracts from the burned HDPE can be associated to the neat gasoline standard over the other two standards. Similarly, the kerosene extracts show higher correlation to the neat kerosene standard than to the neat lighter fluid or neat gasoline standards. However, the lighter fluid extracts cannot be associated to the neat lighter fluid standard; in fact, these extracts show higher correlation to the neat kerosene standard. These results are in agreement with the PCA scores plot in which the gasoline and kerosene extracts were positioned closely to the corresponding standards, while the lighter fluid extracts were positioned closely to the kerosene standards. But, taking into account the chemical composition of the lighter fluid extracts (*i.e.*, dominated by the internal standard, showing few compounds from lighter fluid, and containing the normal alkanes present in kerosene), the positioning of these extracts on the scores plot and the lower PPMC coefficients are not unexpected.

Burned Carpet Padding

Pearson product moment correlation coefficients calculated for comparison of the liquids extracted from the burned carpet padding to the various liquid standards are summarized in Table 4. For gasoline, each extract is strongly correlated to the corresponding standard. Furthermore, the neat and 10% evaporated gasoline extracts are strongly correlated to the neat gasoline standard while the 90% evaporated gasoline extract is moderately correlated. This lower correlation is primarily due to the difference

Table 4. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from burned carpet padding correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from burned carpet padding	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.852 ± 0.042	0.281 ± 0.033	0.852 ± 0.042	0.310 ± 0.045
10% evaporated gasoline	0.854 ± 0.048	0.263 ± 0.047	0.834 ± 0.056	0.279 ± 0.059
90% evaporated gasoline	0.912 ± 0.019	0.331 ± 0.011	0.659 ± 0.021	0.393 ± 0.018
Neat kerosene	0.772 ± 0.082	0.558 ± 0.039	0.532 ± 0.067	0.772 ± 0.082
10% evaporated kerosene	0.557 ± 0.084	0.423 ± 0.050	0.398 ± 0.062	0.608 ± 0.089
70% evaporated kerosene	0.360 ± 0.049	0.318 ± 0.036	0.344 ± 0.050	0.465 ± 0.056
Neat lighter fluid	0.374 ± 0.033	0.374 ± 0.033	0.235 ± 0.033	0.259 ± 0.040
10% evaporated lighter fluid	0.512 ± 0.067	0.517 ± 0.068	0.304 ± 0.056	0.356 ± 0.072
90% evaporated lighter fluid	0.596 ± 0.064	0.591 ± 0.048	0.330 ± 0.035	0.421 ± 0.048

in chemical composition between the 90% evaporated extract and the neat standard (*i.e.*, loss of toluene), as well as the presence of matrix interferences in the extract. Each of the gasoline extracts shows only weak correlation to the neat lighter fluid and neat kerosene standards, allowing association of the extract to the appropriate standard. While the presence of matrix interferences affects the PPMC coefficient, some of the interferences from carpet padding co-elute with compounds in already present in gasoline: styrene and phenol from the matrix co-elute with *o*-xylene and *o*-ethyltoluene, respectively, in gasoline). Hence, gasoline is less affected by these interferences than the other two liquids.

The neat and 10% kerosene extracts are moderately correlated to the corresponding standard, which can be attributed to the presence of interferences from the carpet padding that are only present in the extract. There is only weak correlation between the 70% evaporated extract and standard which is not only due to interferences present in the extract, but also due to the higher background in the 70% evaporated kerosene standard, as described previously. With the exception of the 70% evaporated extract, the kerosene extracts show moderate to weak correlation to the neat lighter fluid and neat gasoline standards but moderate correlation to the neat kerosene standard. The 70% evaporated extract shows weak correlation to all three neat standards; however, the coefficient is higher (0.465) for comparison to the neat kerosene compared to the neat lighter fluid and neat gasoline standards (0.318 and 0.344, respectively). Thus, based on PPMC coefficients, the neat and 10% evaporated kerosene standards can be associated to the appropriate liquid although this association is less well defined for the 70% evaporated extract.

The neat lighter fluid extract is only weakly correlated to the corresponding standard, while the 10% evaporated and 90% evaporated extracts are moderately correlated to the corresponding standard. The lower coefficients are due to the presence of interferences from the carpet padding, as expected. However, in the neat lighter fluid extract, some of these interferences are also misaligned, which lowers the coefficient even further. When compared to the neat lighter fluid standard, the neat lighter fluid extract is only weakly correlated, while the 10% and 90% evaporated extracts are moderately correlated. However, all three extracts are only weakly correlated to the neat gasoline and kerosene standards. In this case, association of the 10% and 90% evaporated lighter fluid extracts to the appropriate liquid is possible using PPMC coefficients. Currently, association of the neat lighter fluid extract to the appropriate liquid is not possible; however, this is primarily due to retention time misalignments that result in the low PPMC coefficient.

Effect of matrix interferences and thermal degradation on association of simulated ignitable liquid residues to corresponding liquid standard using PCA

Replicate samples of each unburned matrix were spiked with each of the undiluted liquid standards. The spiked matrices were burned for the previously specified time, to generate simulated ignitable liquid residues (ILRs), then extracted and analyzed by GC-MS as described previously. The resulting TICs were subjected to the same data pretreatment procedures as before and the appropriate set of liquid standards was analyzed using PCA to generate eigenvectors for the data set. Scores for each simulated

ILR were calculated as described previously and then projected onto the appropriate scores plot.

Simulated ILRs for Carpet

The scores plot with scores projected for the simulated ILRs for the carpet matrix is shown in Figure 9. There is substantial spread among replicate extractions of each liquid, particularly for the ILRs containing kerosene. However, this spread is due to the inherent variability associated with both the burning and thermal degradation processes.

The gasoline-containing ILRs are generally positioned very closely to the gasoline standards. As mentioned previously, only matrix interferences that are either present in the liquid standards or that elute at similar retention time to compounds in the standards will affect positioning of the ILRs on the scores plot. For the carpet ILRs, the major interference is styrene, which co-elutes with *o*-xylene, one of the C_2-alkylbenzenes in gasoline. Hence, the introduction of styrene as an interference does not significantly shift positioning of the gasoline ILRs compared to the standards. Replicates of one 90% evaporated gasoline ILR are positioned more positively on both PCs in the scores plot compared to the standard. When the mean-centered data are considered, the internal standard in these replicates is positive. Since the internal standard is weighted positively on both PC1 and PC2, the product of the eigenvector and mean-centered data is positive at this retention time, resulting in the more positive positioning of these replicates in the scores plot.

In general, the simulated ILRs containing neat kerosene and 10% evaporated kerosene are positioned more negatively on both PCs in the scores plot, compared to the

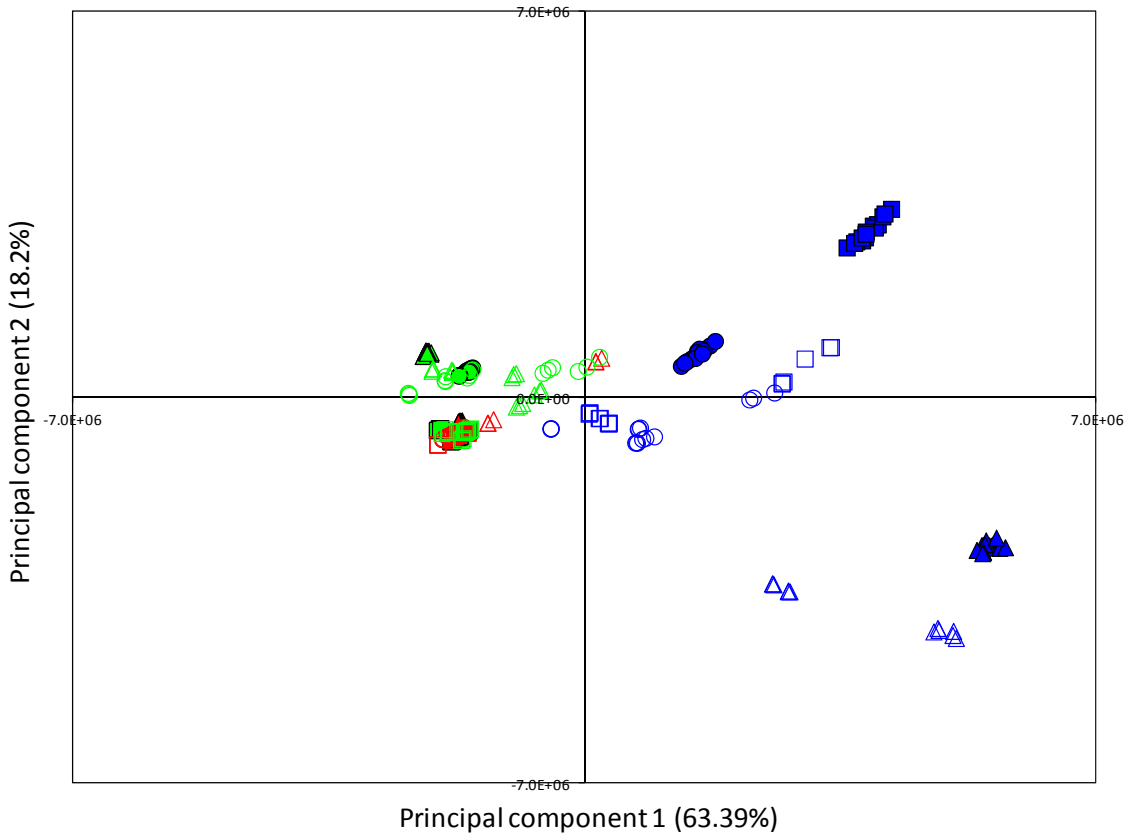

Figure 9. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the simulated ignitable liquid residues from the carpet matrix. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

corresponding standards. In both cases, the internal standard is positive in the mean-centered data for the standard but negative in the mean-centered data for the ILR. Since the internal standard is weighted positively on both PC1 and PC2, then the product of the eigenvector and mean-centered data is positive for the standard but negative for the ILR. As a result, the neat and 10% evaporated kerosene ILRs are positioned more negatively on both PCs than the corresponding standards.

The 70% evaporated kerosene ILR contains significant contributions from the matrix, namely styrene. In the mean-centered data for this ILR, styrene is positive although has a negative contribution to both PC1 and PC2. Hence, the product of the mean-centered data and eigenvector is negative for both PCs, resulting in the more negative positioning of this ILR in the scores plot compared to the corresponding standard.

The simulated ILRs containing neat lighter fluid are positioned very closely to the neat lighter fluid standard, as well as to the neat gasoline standard. This positioning is not surprising due to the abundance of styrene in the neat lighter fluid ILRs. Since styrene co-elutes with one of the characteristic gasoline compounds, styrene will affect positioning of the ILRs on the scores plot. In this case, the presence of styrene results in the ILRs appearing more similar to gasoline and hence, shifting toward the gasoline standards.

Although styrene is also present in the simulated ILRs containing 10% evaporated lighter fluid, the positioning of these ILRs is more affected by misalignment of the internal standard in the ILR. In the mean-centered data, the internal standard is negative in replicates of three ILRs but positive in replicates of two ILRs. The internal standard is positive in the eigenvectors for both PC1 and PC2 such that the product of the mean-

centered data and eigenvector is negative on both PCs for three ILRs but positive on both PCs for two ILRs. This is apparent in the scores plot in which replicates of three ILRs are positioned more negatively than the corresponding standard, while replicates of the other two ILRs are positioned more positively.

The simulated ILRs containing 90% evaporated lighter fluid are positioned more positively on PC1 and more negatively on PC2 in the scores plot compared to the corresponding standard. The ILRs do not contain C_9, contain a lower abundance of C_{10} than the standard, but a greater abundance of C_{11} compared to the standard. Since C_9 and C_{10} are weighted negatively on PC1 and C_{11} is weighted positively, the lower abundance of C_{10} and the higher abundance of C_{11} in the ILR result in an overall more positive position on PC1 in the scores plot compared to the standards. The three alkanes are weighted positively on PC2; however, the abundance of C_{10} is approximately double in the standard compared to the ILR. Hence, C_{10} dominates the positioning of the 90% evaporated lighter fluid in the scores plot. Since the ILR contains a lower abundance of C_{10}, it is positioned less positively (*i.e.*, more negatively) on PC2 in the scores plot compared to the standard.

Based on the scores plot alone, association of the gasoline ILRs to the appropriate standard is possible. However, due to spread among replicates of the kerosene- and lighter fluid-containing ILRs, it is not possible to confidently associate these ILRs to the corresponding liquid. In general, these ILRs are shifted more toward the gasoline standards, most likely due to the presence of styrene as an interference, which co-elutes with xylene, one of the C_2-alkylbenzenes in gasoline.

Simulated ILRs for HDPE

The scores plot for the liquid standards with projections for the simulated ILRs for the HDPE matrix is shown in Figure 10. The gasoline simulated ILRs are positioned similarly to the corresponding standards on PC1 in the scores plot. On PC2, the neat and 10% evaporated gasoline ILRs are positioned more negatively due to the addition of the normal alkane matrix interferences from the HDPE.

In the corresponding loadings plots (data not shown), these alkanes are weighted negatively on both PCs although have a very low contribution to PC1. Hence, the positioning of these extracts in the scores plot is more affected on PC2. Replicates of one extract of the neat gasoline simulated ILR are positioned more positively on PC2 in the scores plot than the standard and other ILRs. This particular ILR has a greater abundance of toluene and the C_2-alkylbenzenes compared to the other neat gasoline ILRs. These compounds have low contribution to PC1 and hence, positioning of the ILRs is not as affected on PC1. However, on PC2, these compounds have greater contribution and are weighted positively, thereby positioning replicates of this ILR more positively on PC2 in the scores plot than those of the other four ILRs containing neat gasoline.

The 90% evaporated gasoline ILRs are positioned more negatively on PC2 in the scores plot than the corresponding standard, which is due to the addition of normal alkanes interferences from the HDPE matrix. While the alkanes are weighted negatively on both PCs, these compounds have low contribution to PC1. Hence, positioning of the 90% gasoline simulated ILRs is not as affected on PC1. However, the more negative weighting of the normal alkanes on PC2 results in the ILRs being positioned more negatively than the corresponding standard on this PC in the scores plot.

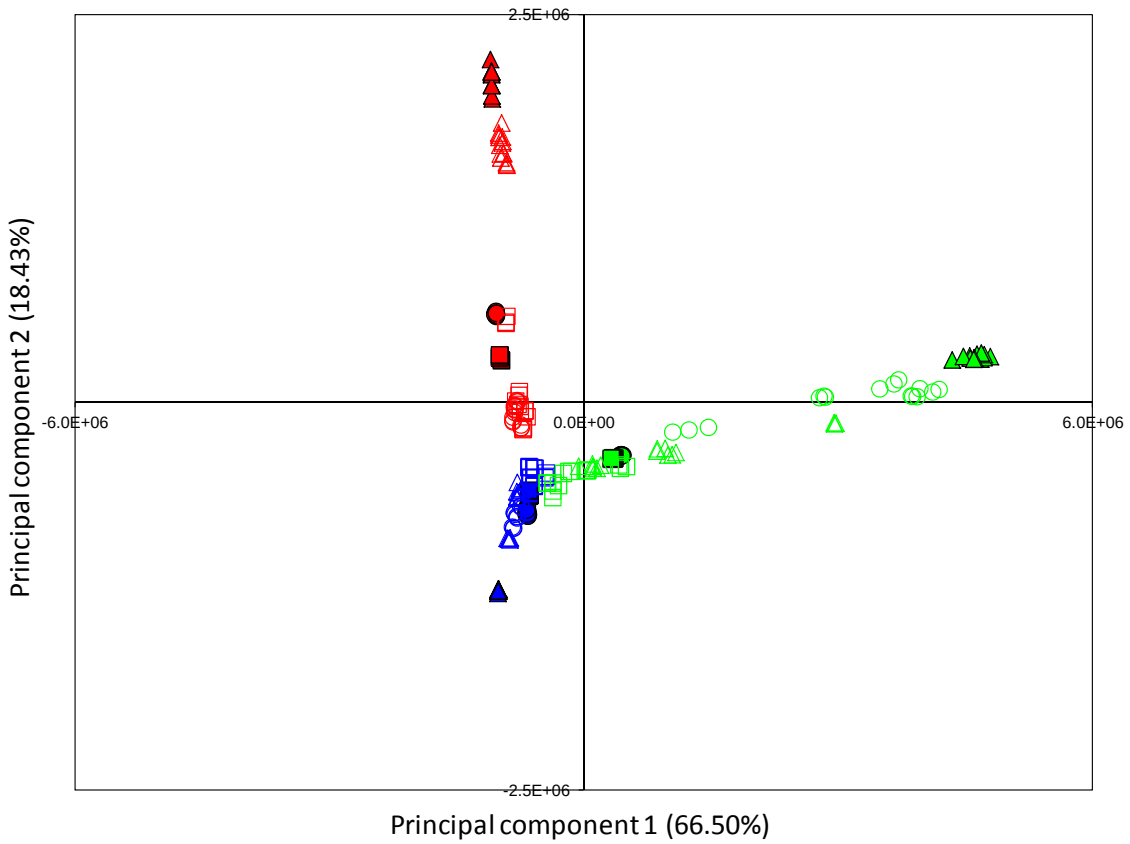

Figure 10. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the simulated ignitable liquid residues from the high density polyethylene matrix. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

The simulated ILRs containing kerosene are also positioned closely to the corresponding standards in the scores plot, although are slightly more positive on PC2. This is due to the additional presence of toluene as a matrix interference. Toluene is not only used during production of HDPE, but is also a degradation product of polyethylene. Since toluene is a compound in gasoline, the presence of this compound will affect positioning of the ILRs on the scores plot. And, since toluene is weighted positively on PC2, the ILRs are positioned more positively on this PC in the scores plot.

The neat lighter fluid ILRs are positioned more negatively on PC1 to the corresponding standard, and similarly on PC2, in the scores plot. The dominant compounds in lighter fluid (C_9, C_{10}, and C_{11}) are all weighted positively on PC1. The neat lighter fluid ILR contains greater abundance of C_{11} than the standard, although the abundance of C_{10} is higher in the standard than in the ILR. Since C_{10} dominates the loadings plot, the lower abundance of this compound in the ILR results in a less positive (*i.e.*, more negative) position in the scores plot. Although the ILR also contains normal alkanes from the matrix, these compounds have low contribution to PC1 and hence, do not substantially affect positioning of the ILR on this PC.

The opposite argument can be made to explain the slightly more negative positioning of the lighter fluid ILR compared to the standard on PC2 in the scores plot. In this case, the lighter fluid compounds have little contribution to PC2 while the normal alkanes from the matrix have greater contribution. Thus, the presence of the matrix interferences in the simulated ILRs containing neat lighter fluid results in the more negative positioning of the ILRs on this PC, compared to the standard.

The simulated ILRs containing 10% evaporated lighter fluid are positioned more positively on both PCs in the scores plot compared to the corresponding standard. The ILRs contain a substantially greater abundance of C_9, C_{10}, and C_{11} than the standard. Since these three compounds are weighted positively on PC1, the higher abundance results in a more positive score on this PC for the simulated ILRs. On PC2, C_9 has a negative, while C_{10} has a positive, contribution. In addition, the normal alkanes present as matrix interferences also have a negative contribution on PC2. However, C_{10} dominates in the ILRs, resulting in an overall positive score on PC2 compared to the standard. There is also substantial spread among extracts of the simulated ILRs containing 10% evaporated lighter fluid. This is mainly due to the varying abundance of the lighter fluid compounds among replicates of the ILRs.

The 90% evaporated lighter fluid ILR is positioned more negatively on both PC1 and PC2 in the scores plot, compared to the corresponding standard. The ILRs and standards have similar abundance of C_9, while C_{10} and C_{11} are present in lower abundance in the ILRs. Overall, there is less positive contribution on PC1, resulting in the ILRs being positioned more negatively than the corresponding standard on this PC in the scores plot. On PC2, the more negative positioning is mainly due to the presence of the normal alkane matrix interferences that are present in the ILR but not the standard.

Simulated ILRs for Carpet Padding

The scores plot with projections for the simulated ILRs for the carpet padding matrix is shown in Figure 11. Positioning of the ILRs relative to the standards is generally similar to that observed in the previous section for the liquids extracted from

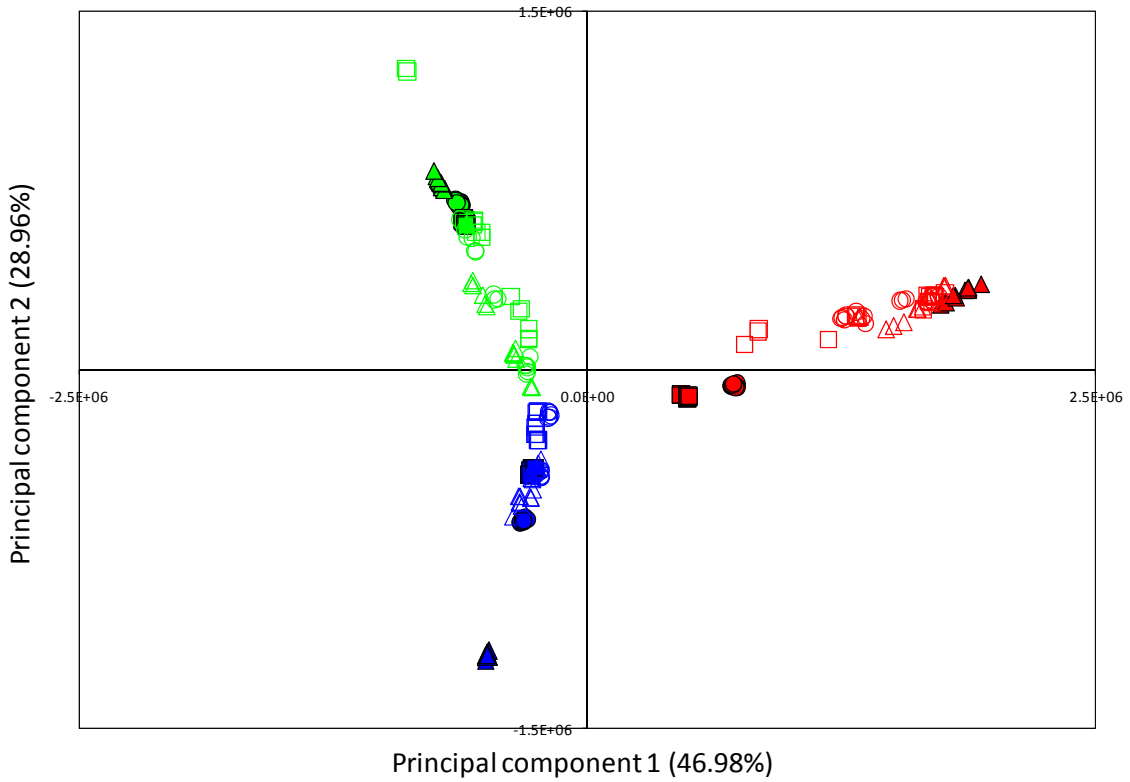

Figure 11. Scores plot of principal component 1 versus principal component 2 based on total ion chromatograms for the nine ignitable liquid standards with scores projected for the simulated ignitable liquid residues from the carpet padding matrix. Standards are represented by filled symbols while the corresponding extract is represented by the open symbol. Gasoline is shown in red, kerosene in blue, and lighter fluid in green. Symbols denote level of evaporation as follows: squares indicate the neat liquid, circles indicate the 10% evaporated liquid, and triangles represent 90% evaporation for gasoline and lighter fluid and 70% evaporation for kerosene.

the burned carpet padding (Figure 8). However, in the case of the ILRs, there is substantial spread among replicates, as is expected due to the variable nature of the burning and thermal degradation processes.

The neat and 10% evaporated gasoline ILRs are positioned more positively on both PCs in the scores plot compared to the corresponding standards. As before, this is primarily due to the greater abundance of the C_2- and C_3-alkylbenzenes in the ILRs compared to the standards. The ILR containing 90% evaporated gasoline is positioned similarly to the corresponding standard on both PCs in the scores plot, which is due to the similar abundance of the characteristic gasoline compounds in the ILR and standard.

While spread is expected among replicates, it is perhaps most apparent among replicates of the ILR containing neat gasoline. This is due to misalignment of the co-eluting styrene and *o*-xylene peaks in the TIC. As mentioned previously, only compounds present in the standards, or which elute at the same retention time as compounds in the standards, will affect positioning of the ILRs in the scores plot. In the standards, *o*-xylene elutes at 5.68 minutes. However, due to the afore-mentioned misalignment, the *o*-xylene peak elutes at 5.62 minutes for four of the 15 neat gasoline ILRs. As a result, the contribution of *o*-xylene in these four replicates is not fully taken into account when calculating the scores and results in the difference in position (*i.e.*, spread) observed among the replicates. This misalignment is also present in the 10% and 90% evaporated extracts and can be used in a similar manner to explain the spread observed among replicates of these ILRs.

The simulated ILRs containing kerosene are positioned similarly on PC1 in the scores plot, but more positively on PC2, than the corresponding standards. As described

previously for the burned carpet padding, the difference in positioning is primarily due to differences in abundance of the characteristic kerosene compounds between the standards and the simulated ILRs. The normal alkanes are present in lower abundance in the ILRs than the standards: since the alkanes are weighted negatively on PC2, the lower abundance results in a less negative (*i.e.*, more positive) positioning of the ILRs in the scores plot. And, since the alkanes have greater contribution to PC2, positioning of the ILRs is more affected on PC2 than on PC1.

The lighter fluid-containing ILRs are generally positioned similarly on PC1, but more negatively on PC2, than the corresponding standards in the scores plot. Among replicates of each ILR, there is substantial variability in the abundance of the characteristic lighter fluid compounds. In some cases, replicates contain higher abundance than the standard but overall, abundances are higher in the standard than the ILR. As a result, the ILRs are positioned less positively (*i.e.*, more negatively) than the standards in the scores plot. And, since the C_9-C_{11} normal alkanes have greater contribution to the variance described by PC2, positioning of the ILRs is more affected on PC2 than on PC1.

Three replicates of the ILR containing neat lighter fluid are actually positioned more positively on PC2 than the standards and other ILRs. Again, this difference in positioning is due to differences in abundance, specifically of the C_{10} normal alkane. In the neat lighter fluid standard, the abundance of C_{10} is approximately 5.2×10^5. In the corresponding ILRs, the abundance of this compound ranges from approximately 1.5×10^5 to 9.2×10^5. Since C_{10} dominates the loadings for PC2 (positive weighting), the ILR

replicates that contain the greatest abundance of C_{10} (~9.2 x 10^5) are positioned most positively on PC2.

Thus, based on visual assessment of the scores plot, it is possible to associate gasoline- and kerosene-containing ILRs to the appropriate liquid type, although not to an actual evaporation level. In contrast, ILRs containing lighter fluid are more difficult to associate since the ILRs are positioned between the lighter fluid and kerosene standards.

Effect of matrix interferences and thermal degradation on association of simulated ignitable liquid residues to corresponding liquid standard using PPMC coefficients

Pearson product moment correlation coefficients were also calculated to assess association of each simulated ILR for each matrix to the corresponding liquid standard, as well as to the neat liquid standards.

Simulated ILRs for Carpet

Calculated PPMC coefficients for comparisons of the simulated ILRs for the carpet matrix are summarized in Table 5. Standard deviations associated with the mean are high due to variability not only in burning but also in thermal degradation occurring as the liquid and matrix burn. Each simulated ILR is weakly to moderately correlated to the corresponding standard. These lower coefficients are primarily due to the presence of the matrix interferences that are present in the ILR but not the standard.

The simulated ILRs containing gasoline are more strongly (based on higher coefficients) correlated to the neat gasoline standard than to the neat lighter fluid or kerosene standards. The one exception is the 90% evaporated gasoline ILR for which

Table 5. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from the simulated ignitable liquid residue for the carpet matrix correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from simulated ILR	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.712 ± 0.061	0.398 ± 0.077	0.712 ± 0.061	0.627 ± 0.094
10% evaporated gasoline	0.685 ± 0.032	0.324 ± 0.045	0.676 ± 0.038	0.535 ± 0.071
90% evaporated gasoline	0.650 ± 0.137	0.243 ± 0.127	0.422 ± 0.102	0.512 ± 0.096
Neat kerosene	0.665 ± 0.101	0.130 ± 0.063	0.124 ± 0.080	0.665 ± 0.101
10% evaporated kerosene	0.800 ± 0.067	0.131 ± 0.124	0.150 ± 0.146	0.684 ± 0.108
70% evaporated kerosene	0.794 ± 0.157	0.123 ± 0.226	0.158 ± 0.248	0.485 ± 0.148
Neat lighter fluid	0.612 ± 0.145	0.612 ± 0.145	0.507 ± 0.083	0.638 ± 0.064
10% evaporated lighter fluid	0.711 ± 0.122	0.705 ± 0.107	0.381 ± 0.216	0.535 ± 0.194
90% evaporated lighter fluid	0.514 ± 0.313	0.550 ± 0.089	0.407 ± 0.227	0.557 ± 0.138

there is only weak correlation to the neat gasoline standard. This lower coefficient is due not only to the presence of interferences in the ILR but also due to the chemical differences between 90% evaporated gasoline and neat gasoline, which are a result of evaporative losses.

The simulated ILRs containing kerosene show moderate (within one standard deviation) correlation to the neat kerosene standard, but only weak correlation to the neat lighter fluid and neat gasoline standards. Hence, kerosene-containing ILRs are readily associated to the corresponding liquid type. The lighter fluid ILRs show moderate correlation to the corresponding standard, weak to moderate correlation to the neat gasoline, and moderate correlation to the neat kerosene standard. Thus, association of lighter fluid ILRs to the lighter fluid standards is not possible based on PPMC coefficients

In summary, using both PCA and PPMC, it is possible to associate simulated ILRs containing gasoline and kerosene to the corresponding standard although not necessarily to the specific evaporation level. However, association of simulated ILRs containing lighter fluid in a similar manner is not possible. This may be due to the three characteristic compounds (C_9, C_{10}, and C_{11}) being relatively volatile in nature and, hence, easily lost during evaporation and burning.

Simulated ILRs for HDPE

The calculated PPMC coefficients are summarized in Table 6. Moderate to strong correlation is observed for comparison of each simulated ILR to the corresponding standard. This slightly lower correlation is due not only to the presence of matrix interferences in the ILRs, but also to the effects of evaporation and thermal degradation that occur during the burning process.

The simulated ILRs containing gasoline show weak correlation to the neat lighter fluid standard but moderate correlation to neat gasoline, and weak to moderate correlation to kerosene. This higher correlation to kerosene results from the addition of the normal alkanes as matrix interferences in the simulated ILR. Despite moderate correlation to both gasoline and kerosene standards, the actual coefficients are higher for comparison to the neat gasoline standard. Thus, in combination with PCA, it is possible to more closely associate the simulated ILRs containing gasoline to the gasoline standard, rather than to the kerosene standard.

Kerosene-containing simulated ILRs show moderate to strong correlation to the corresponding standards, which is expected due to additional evaporative losses and thermal degradation that occur during burning. The kerosene ILRs show only weak correlation to the neat lighter fluid and neat gasoline standards, but moderate to strong correlation to the neat kerosene standard. Therefore, association to the corresponding standard is also possible for these simulated ILRs, mainly because the matrix interferences are compounds that are also characteristic of this liquid and, hence, are present in both the standard and the ILR.

Table 6. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from the simulated ignitable liquid residue for the HDPE matrix correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from simulated ILR for HDPE matrix	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.636 ± 0.105	0.393 ± 0.087	0.636 ± 0.105	0.544 ± 0.148
10% evaporated gasoline	0.715 ± 0.059	0.483 ± 0.045	0.735 ± 0.071	0.696 ± 0.074
90% evaporated gasoline	0.937 ± 0.037	0.280 ± 0.006	0.633 ± 0.025	0.380 ± 0.018
Neat kerosene	0.817 ± 0.055	0.456 ± 0.058	0.432 ± 0.091	0.817 ± 0.055
10% evaporated kerosene	0.874 ± 0.050	0.365 ± 0.064	0.413 ± 0.068	0.853 ± 0.058
70% evaporated kerosene	0.751 ± 0.130	0.370 ± 0.113	0.406 ± 0.119	0.766 ± 0.058
Neat lighter fluid	0.728 ± 0.082	0.728 ± 0.082	0.414 ± 0.125	0.675 ± 0.137
10% evaporated lighter fluid	0.841 ± 0.048	0.828 ± 0.040	0.202 ± 0.141	0.369 ± 0.227
90% evaporated lighter fluid	0.721 ± 0.145	0.669 ± 0.061	0.327 ± 0.141	0.632 ± 0.187

The lighter fluid simulated ILRs show moderate correlation to the corresponding standards, which again, is expected due to evaporative losses and thermal degradation during burning, as well as the additional presence of matrix interferences. The lighter fluid ILRs show moderate to strong correlation to the neat lighter fluid standard, weak correlation to the neat gasoline standard, and moderate to weak correlation to the neat kerosene standard. This slightly higher correlation to kerosene is again due to the normal alkanes that are present as matrix interferences in the ILRs, as well as their presence as characteristic compounds in kerosene. Thus, it is possible to associate the simulated ILRs containing lighter fluid to the corresponding liquid using PPMC coefficients.

Simulated ILRs for Carpet Padding

The mean PPMC coefficients calculated between each simulated ILR and the corresponding standard, as well as similarity to the neat lighter fluid, neat gasoline, and neat kerosene standards, are summarized in Table 7. Simulated ILRs containing neat and 10% evaporated gasoline show moderate correlation to the corresponding standard, while the ILRs containing 90% evaporated gasoline show strong correlation. In calculating PPMC coefficients, the presence of matrix interferences lowers the coefficient. While matrix interferences contribute to the lower coefficients for all gasoline ILRs and corresponding standards, there is an additional contribution from misalignments of the co-eluting styrene and *o*-xylene peaks in the TICs, particularly for the ILRs containing neat and 10% evaporated gasoline. When compared to the neat standards of the three liquids, the gasoline ILRs are moderately correlated to neat gasoline, but are

Table 7. Mean Pearson product moment correlation coefficients for replicates (n=225) of each liquid extracted from the simulated ignitable liquid residue for the carpet padding matrix correlated to the corresponding standard, the neat lighter fluid standard, the neat gasoline standard, and the neat kerosene standard.

Liquid extracted from simulated ILR for carpet padding matrix	Mean PPMC coefficient ± standard deviation			
	Corresponding standard	Neat lighter fluid standard	Neat gasoline standard	Neat kerosene standard
Neat gasoline	0.766 ± 0.055	0.316 ± 0.062	0.766 ± 0.055	0.360 ± 0.087
10% evaporated gasoline	0.747 ± 0.032	0.302 ± 0.033	0.733 ± 0.032	0.344 ± 0.053
90% evaporated gasoline	0.951 ± 0.024	0.281 ± 0.033	0.573 ± 0.033	0.419 ± 0.042
Neat kerosene	0.626 ± 0.097	0.447 ± 0.033	0.451 ± 0.054	0.626 ± 0.097
10% evaporated kerosene	0.696 ± 0.137	0.405 ± 0.057	0.408 ± 0.079	0.724 ± 0.092
70% evaporated kerosene	0.582 ± 0.066	0.394 ± 0.025	0.446 ± 0.059	0.672 ± 0.034
Neat lighter fluid	0.518 ± 0.140	0.518 ± 0.140	0.272 ± 0.060	0.319 ± 0.052
10% evaporated lighter fluid	0.478 ± 0.158	0.481 ± 0.155	0.280 ± 0.043	0.327 ± 0.064
90% evaporated lighter fluid	0.519 ± 0.125	0.498 ± 0.062	0.338 ± 0.055	0.448 ± 0.027

only weakly correlated to neat lighter fluid and neat kerosene. Hence, association of the ILRs to gasoline is possible, albeit not to the specific evaporation level.

The kerosene ILRs are all moderately correlated to the corresponding standard. Again, the presence of matrix interferences in the ILR, but not the standard, results in the lower coefficients. The kerosene ILRs are moderately correlated to the neat kerosene standard but only weakly associated to the neat lighter fluid and neat gasoline standards. Thus, using PPMC coefficients, association of kerosene-containing ILRs to the appropriate liquid type is possible, but not to the specific evaporation level.

The lighter fluid ILRs show weak to moderate correlation to the corresponding standard. However, the standard deviation associated with the PPMC coefficients is large, due to the variable burning of the volatile compounds in this liquid. When the standard deviation is taken into account, the ILRs are all moderately correlated to the corresponding standard. The ILRs are moderately correlated (within one standard deviation) to the neat lighter fluid standard, but only weakly correlated to the neat gasoline and neat kerosene standards. Hence, association of the ILRs to lighter fluid standards is also possible, using PPMC coefficients.

Summary

Using PCA, differentiation of the liquid standards was possible according to liquid type (gasoline, lighter fluid, and kerosene), which was expected due to distinct differences in chemical composition among the liquids.

In this research, PCA was performed initially on the liquid standards alone and the resulting eigenvectors were then used to calculate scores for the simulated ILRs.

Conducting PCA in this manner ensures that similarities and differences among samples are chemical in nature, rather than artifacts of the burning, extraction, and analysis procedures. Furthermore, only compounds present in the eigenvectors will affect positioning of the simulated ILRs on the scores plot; that is, only compounds present in both the liquid standards and ILRs will affect positioning of the latter. As a result, when used in this manner, PCA is essentially a filter that minimizes or eliminates the effect of matrix interferences.

Using PCA in this manner, it was generally possible to associate liquids extracted from the burned matrix and the simulated ILRs according to liquid type. In some cases, however, association to the appropriate liquid was not possible, based on visual assessment of the scores plot. This was primarily due to the difference in abundance of the characteristic compounds in the extract and corresponding standard. In addition, matrix interferences in the HDPE matrix consisted of normal alkanes, which are characteristic compounds in kerosene. Since these compounds were present in the liquid standards, their presence did affect positioning of extracts on the scores plot. This meant that the gasoline and lighter fluid extracts were shifted toward the kerosene standards in the scores plot, making association to the corresponding liquid more difficult.

Throughout this research, PPMC coefficients were also calculated to assess association of the extract or simulated ILR and corresponding standards. Coefficients were used to assess similarity between two chromatograms, based on all data points in the chromatograms. This is in contrast to PCA, which identifies differences among samples based on a reduced number of variables. However, unlike PCA, the calculated PPMC coefficients were affected by the presence of interferences. For two

chromatograms being compared point-by-point, the presence of interferences in one chromatogram but not the other lowered the PPMC coefficient. Despite these issues, however, it was generally possible to associate the extracts to the corresponding neat standard using PPMC coefficients.

In summary, using the combination of PCA and PPMC coefficients, association of the extracts and simulated ILRs to the corresponding liquid type was possible, albeit not to the specific evaporation level. While these statistical procedures show promise for application in forensic laboratories, a wider variety of substrates and the associated thermal degradation or pyrolysis products must be investigated in a similar manner. Additionally, the potential of supervised statistical procedures, which build models and thus, can be used to predict classification of simulated ILRs, should be investigated in a similar manner. The next direction of this research will investigate such a supervised procedure, namely a soft independent modeling of class analogy (SIMCA) approach, and we are currently comparing different statistical software packages for this purpose.

Publications

K.R. Prather, V.L. McGuffin, and R. Waddell Smith. Effect of Evaporation and Matrix Interferences on the Association of Simulated Ignitable Liquid Residues to the Corresponding Liquid Standard. *Forensic Science International.* In review.

K.R. Prather, S.E. Towner, V.L. McGuffin, and R. Waddell Smith. Effect of Interferences from High Denisty Polyethylene on Association of Simulated Ignitable Liquid Residues to the Corresponding Liquid. In preparation for submission to *Journal of Forensic Sciences*.

Presentations

K.R. Prather, S.E. Towner, V.L. McGuffin, and R. Waddell Smith. *Effects of Matrix Interference, Weathering, and Thermal Degradation on the Association of Ignitable Liquid Residues to Neat Ignitable Liquids.* Oral presentation at the 63rd Annual Meeting of the American Academy of Forensic Sciences, Chicago, IL. February 2011.

K.R. Prather, V.L. McGuffin, and R. Waddell Smith. *Analysis of Fire Debris using Gas Chromatography-Mass Spectrometry and Multivariate Statistical Procedures.* Poster presentation at the 3rd Annual Graduate Academic Conference, Michigan State University, East Lansing, MI. March 2011.

K.R. Prather, S.E. Towner, V.L. McGuffin, and R. Waddell Smith. *Using Multivariate Statistical Procedures to Identify Ignitable Liquid Residues in the Presence of Interferences.* Oral presentation at the 42nd Central Regional Meeting of the American Chemical Society, Indianapolis, IN. June 2011.

S.E. Towner, K.R. Prather, V.L. McGuffin, and R. Waddell Smith. *Effect of Evaporation, Matrix Interferences, and Thermal Degradation on the Association and Discrimination of Ignitable Liquids Extracted from High Density Polyethylene.* Poster presentation at the 40th Annual Meeting of the Midwestern Association of Forensic Scientists, Chicago, IL. September 2011.

K.R. Prather, S.E. Towner, V.L. McGuffin, and R. Waddell Smith. *Investigating the Use of Multivariate Statistical Procedures in Fire Debris Analysis.* To be presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Orlando, FL. March 2012.