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PAPER

CRIMINALISTICS

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Association of Ignitable Liquid Residues to Neat Ignitable Liquids in the Presence of Matrix Interferences Using Chemometric Procedures*,†

ABSTRACT: In fire debris analysis, weathering of ignitable liquids and matrix interferences can make the identification of ignitable liquid residues (ILRs) difficult. An objective method was developed to associate ILRs with the corresponding neat liquid with discrimination from matrix interferences using principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients. Six ignitable liquids (gasoline, diesel, ultra pure paraffin lamp oil, adhesive remover, torch fuel, paint thinner) were spiked onto carpet, which was burned, then extracted using passive headspace extraction, and analyzed by gas chromatography-mass spectrometry. Both light and heavy burn conditions were investigated. In the PCA scores plot, ignitable liquids were discriminated based on alkane and aromatic content. All ILRs were successfully associated with the corresponding neat liquid using both PCA and PPMC coefficients, regardless of the extent of burning. The method developed in this research may make the association of ILRs with corresponding neat liquids more objective.

KEYWORDS: forensic science, fire debris analysis, ignitable liquids, gas chromatography-mass spectrometry, principal components analysis, Pearson product moment correlation coefficients

Visual assessment of gas chromatograms for the identification of ignitable liquid residues (ILRs) is notoriously difficult and often subjective, for a number of reasons. The two main problems associated with visual assessment are weathering, or evaporation, of the ignitable liquid and contributions from the fire debris matrix.

In arson cases, volatile components of the ignitable liquid are lost during the burning process. When the ILR is subsequently extracted from the fire debris and analyzed by gas chromatography-mass spectrometry (GC-MS), the resulting chromatogram is different from the chromatogram of the neat liquid. This can make it difficult to successfully identify an ILR based on comparison to a reference collection of neat liquids. Studies in the literature have applied statistical and chemometric procedures to make identification of an ignitable liquid or ILR less subjective. Barnes et al. (1) successfully associated 50% and 75% evaporated gasoline samples with the neat counterpart using ratios of aliphatic components in the isobutene to methylnaphthalene region of the chromatogram. Sandercock and Du Pasquier (2) used principal components analysis (PCA) to classify 35 gasoline samples at different levels of evaporation (25%, 50%, 75%, and 90% evaporated by weight) from 24 service stations. These studies show the potential to objectively associate an ILR back to a neat liquid; however, the effect of matrix interferences on the association was not investigated.

Fire debris matrices from which ILRs are routinely extracted, such as clothing, carpet or upholstery, often contain hydrocarbons that are also present in ignitable liquids. Chromatograms of unburned and burned matrices can be similar to that of an ignitable liquid as a result of peaks from inherent hydrocarbons, thermal degradation, or pyrolysis products. These products can complicate the chromatogram of an ILR and make identification difficult or even mask the presence of the ILR.

Lentini et al. (3) demonstrated potential matrix interferences in a wide range of unburned household products (e.g., furniture polish, terry cloth towel, printed T-shirt, shoes, newspaper, and magazines). Almirall and Furton (4) studied a variety of burned matrices and showed that target compounds for the identification of ILRs, such as alkylbenzenes, naphthalenes, and various hydrocarbons, were often found as combustion or pyrolysis products of burned matrices. However, the authors found that these target compounds were in different ratios in burned matrices than in ignitable liquids. Fernandes et al. (5) investigated the presence of pyrolysis products in 15 different burned household items. However, in each of the aforementioned studies, the matrices were not spiked with an ignitable liquid and thus, the effect of matrix interferences on the identification of an ILR was not demonstrated (3–5).

Few studies are available in the literature in which the effect of evaporation and matrix interferences on the association of an ILR

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with the neat liquid are reported (6–8). Bertsch (6) investigated pyrolysis products obtained from unburned and burned carpet samples and their potential to interfere with the identification of gasoline. In the study, visual assessment of chromatograms showed pyrolysis products, such as alkylbenzenes, naphthalenes, and other aromatic hydrocarbons, in simulated and actual fire debris samples that could interfere with the identification of gasoline. However, using GC-MS with selected ion monitoring (SIM), the ion profiles of the burned carpet and gasoline samples was sufficiently different to allow distinction. Borusiewicz et al. (7) conducted a study examining several factors affecting the detection of an ignitable liquid in fire debris, such as type of ignitable liquid, type of burned matrix, burn time, and air availability. The study investigated five ignitable liquids including gasoline, kerosene, and diesel and three burned matrices (carpet, deciduous wood, and chipboard), which had varying contributions to the chromatogram. Through visual assessment of chromatograms, the authors found that the most important factor in detecting the presence of an ILR was the type of burned material, attributed to the absorbent nature of the matrix. Traces of ignitable liquids were identified in nearly all carpet samples, regardless of burn time, whereas traces were identified in only a few of the deciduous wood samples and in none of the chipboard samples.

Tan et al. (8) applied chemometric procedures, rather than visual assessment of chromatograms, to classify 51 ignitable liquids according to five American Society for Testing and Materials (ASTM) classes and to investigate the effects of the matrix on liquid classification. Using PCA and a soft independent modeling of class analogy (SIMCA) approach, the 51 liquids could be classified according to ASTM class. Fire debris was simulated by spiking each ignitable liquid onto a polyolefin-piled carpet, igniting the carpet, and then extracting the residue with methylene chloride. Extracts were analyzed using GC-MS with SIM to minimize interferences from the matrix (8). The resulting chromatograms were divided into 19 segments and the signal within each segment was summed, generating 19 variables that described the chromatogram. Although all ILRs were successfully classified using SIMCA, the authors neither discussed nor illustrated the interferences present and, hence, the identity and extent of matrix interferences is not known.

In the research presented herein, the effects of both weathering and matrix interferences on the association of an ILR with the neat liquid are addressed concurrently. An objective method for the association is described, using Pearson product moment correlation (PPMC) coefficients and PCA. This objective method builds on previous work by Hupp et al. (9) in which 25 diesel samples from 25 service stations analyzed by GC-MS were differentiated using similar procedures. In the work by Hupp et al., as well as this work, the entire chromatogram was investigated rather than specific regions of the chromatogram, peak ratios, or summed segments of the chromatogram, as in other studies (1,2,8). In this way, the chromatogram is described by 4876 data points, or variables, potentially allowing greater discrimination of samples. Additionally, the full mass scan mode is used, rather than the SIM mode as in other studies (6,8), to avoid losing potentially discriminating information.

In the research reported herein, one ignitable liquid from each of six classes outlined by the ASTM was extracted using a passive headspace extraction with activated carbon strips to more closely follow procedures used in crime laboratories. ILRs were simulated by spiking each ignitable liquid onto samples of nylon carpet and lightly burning the carpet. The ILRs were extracted from the matrix using the same passive headspace extraction procedure. PCA and PPMC coefficients were then used to assess the association of an ILR with the corresponding neat liquid in the presence of minimal matrix interferences. The PPMC coefficients were used for a pairwise comparison of chromatograms, which was useful for assessing the correlation, or similarity, of an ILR with the corresponding neat ignitable liquid. Additionally, PCA was applied to the entire data set to assess the association and discrimination of all samples, and the chemical information obtained from PCA was evaluated in detail. In a second study, the nylon carpet was more heavily burned to increase the contribution of matrix interferences to the chromatogram of the ILR. Again, PPMC coefficients and PCA were used to assess the association of each ILR with the corresponding neat liquid. Finally, a new data set was compiled that included an additional liquid from each of the six ASTM classes. The association of the ILR with the corresponding neat liquid in the presence of liquids from the same class was then assessed in a similar manner using PCA and PPMC coefficients.

Materials and Methods

Sample Collection

In total, 12 ignitable liquids, two from each of six ASTM classes, were investigated for this research (Table 1). Initial studies utilized only six of the liquids: gasoline, diesel, adhesive remover, ultra pure paraffin lamp oil, torch fuel, and paint thinner. The gasoline, diesel, and kerosene samples were collected from service stations in the Lansing, MI area whereas the remaining liquids were collected from local grocery stores, hardware stores, and online

TABLE 1—*Ignitable liquids investigated.*

Ignitable Liquid (brand or manufacturer)	ASTM Class	Major Components
Gasoline 1 (Shell)	Gasoline	Normal alkanes C_9–C_{15}, alkylbenzenes, naphthalenes
Gasoline 2 (Meijer)	Gasoline	Normal alkanes C_9–C_{15}, alkylbenzenes, naphthalenes
Diesel (Sunoco)	Petroleum distillates	Normal alkanes C_9–C_{20}, alkylbenzenes, naphthalenes
Kerosene (Meijer)	Petroleum distillates	Normal alkanes C_7–C_{18}, alkylbenzenes, naphthalenes
Ultra pure paraffin lamp oil (Lamplight farms)	Alkane	Normal alkanes C_{11}–C_{15}
Candle wax lifter (Goo Gone)	Alkane	Normal alkanes C_{14}–C_{18}
Adhesive remover (Goof Off)	Aromatic	Ethylbenzene, *o*-xylene, *p*-xylene
Lacquer thinner (Recochem)	Aromatic	Toluene
Odorless paint thinner (Sunnyside)	Isoparaffinic	Branched alkanes C_7–C_{12}
Fabric protector (Scotch Guard)	Isoparaffinic	Branched alkanes C_5–C_7
Torch fuel (Tiki)	Naphthenic paraffinic	Normal alkanes C_{11}–C_{14}, branched/cyclic alkanes
Lamp oil (Medallion)	Naphthenic paraffinic	Normal alkanes C_{11}–C_{14}, branched/cyclic alkanes

ASTM, American Society for Testing and Materials.

sources. Unused nylon carpet (source unknown) was used as the matrix in all studies.

Neat Ignitable Liquids

Each of the 12 neat ignitable liquids was extracted by passive headspace with activated carbon strips, and the resulting extract was analyzed by GC-MS to identify the major components. Five microliters of neat liquid were spiked onto a 2 × 2 cm piece of Kimwipe (Kimberly-Clark, Irving, TX), which was placed in an unlined paint can (Arrowhead Forensics, Lenexa, KS). One-fourth of an activated carbon strip (Albrayco Technologies, Inc., Cromwell, CT) was suspended in the headspace of the can and the sealed can was heated at 80°C for 4 h. After extraction, the activated carbon strip was removed and eluted with 200 μL of carbon disulfide (spectrophotometric grade; Sigma-Aldrich, St. Louis, MO). The resultant extract was then analyzed by GC-MS. Each neat ignitable liquid was extracted and analyzed in triplicate, resulting in 36 chromatograms.

Minimal Matrix Interferences

Nylon carpet was analyzed using the same passive headspace extraction as the neat liquids to identify potential interferences present in the burned carpet. A 5 × 5 cm piece of unused nylon carpet was burned by applying a blow torch (Benzomatic, Medina, NY) for 10 sec and allowing the carpet to immediately self-extinguish. Then, the burned piece of carpet was extracted by passive headspace extraction, eluted with carbon disulfide, and analyzed by GC-MS. A total of three 5 × 5 cm pieces of carpet were burned, extracted, and analyzed using this procedure.

To simulate ILRs, a 5 × 5 cm piece of nylon carpet was spiked with 750 μL of ignitable liquid then burned by applying a blow torch for 10 sec. For this part of the study, six ignitable liquids were used (gasoline, diesel, adhesive remover, ultra pure paraffin lamp oil, torch fuel, and paint thinner) to create six ILRs. The resulting ILR was extracted by the same passive headspace extraction, eluted with carbon disulfide, and analyzed by GC-MS. Each ignitable liquid was individually spiked onto three separate 5 × 5 cm pieces of carpet, burned, extracted, and analyzed, resulting in a total of 18 chromatograms of simulated ILRs.

Increased Matrix Interferences

The carpet was then burned to a greater extent to increase the contribution of matrix interferences to the ILR chromatogram. A 5 × 5 cm piece of carpet was heavily burned by applying a blow torch to the carpet for 20 sec, then allowed to burn further for 1 min, after the blow torch was removed. The carpet was extinguished, by covering it with a clean beaker, and allowed to cool. Again, a total of three pieces of carpet were burned, extracted, and analyzed to identify the change in components from the lighter burning conditions.

A 5 × 5 cm piece of unburned carpet was spiked with 750 μL of ignitable liquid and then heavily burned to simulate the identification of an ILR in the presence of increased matrix interferences. The same six ignitable liquids as before were used to simulate the ILRs. The resulting ILR was extracted by the same passive headspace extraction procedure, eluted with carbon disulfide, and the extract was analyzed by GC-MS. Again, each ignitable liquid was burned and extracted in triplicate, resulting in a total of 18 chromatograms of simulated ILRs.

GC-MS Analysis

All analyses were performed using an Agilent 6890 gas chromatograph interfaced with an Agilent 5975 mass spectrometer (Agilent Technologies, Santa Clara, CA) and equipped with an Agilent HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The inlet temperature was 250°C and 1 μL of the sample was injected in splitless mode using an Agilent 7683B series automated liquid sampler. The GC temperature program had an initial temperature of 40°C for 3 min, was ramped to 280°C at 10°C/min, and held at 280°C for 4 min. The transfer line between the GC column and the mass spectrometer was maintained at 300°C. The mass spectrometer was equipped with an electron ionization source operating at 70 eV and a quadrupole mass analyzer operating in full scan mode (*m/z* 50–550) at a scan rate of 2.91 scans/sec.

Data Analysis

Three data sets were generated throughout this research: the first contained the six neat liquids and six ILRs with minimal interferences, the second contained the six neat liquids and six ILRs with increased interferences, and the third contained the 12 neat liquids and six ILRs with increased interferences. For each data set, total ion chromatograms (TICs) of the neat ignitable liquids, burned carpet, and ILRs were retention time aligned using LineUp™ (version 3.0; Infometrix, Bothell, WA). Matlab (version 7.4.0.287; MathWorks, Natick, MA) was used to calculate PPMC coefficients of aligned chromatograms. In general, PPMC coefficients above 0.8 indicate a strong correlation, between 0.5 and 0.8 indicate a moderate correlation, below 0.5 indicate a weak correlation, and close to 0 indicate no correlation (10). After retention time alignment, chromatograms were peak area normalized to account for variations in injection volume and instrument sensitivity. For normalization, the total area under each chromatogram as well as an average total area was calculated. Then, a normalized chromatogram was generated by dividing each data point in the chromatogram by the total area under the chromatogram, then multiplying it by the average total area.

In addition to PPMC coefficients, PCA was performed. Whereas PPMC coefficients measure the similarity between two chromatograms, PCA highlights differences among samples and magnifies those differences. As such, PPMC coefficients and PCA can be considered complementary. Initially, PCA was performed in Matlab by eigenanalysis of the covariance matrix of the data set containing the neat ignitable liquids, ILRs, and burned carpet. By including the ILRs and burned carpet, PCA identified the differences introduced by burning as well as the differences among the liquids. Although performing PCA in this way demonstrated the robustness of the method, a second method was investigated that would be more applicable in a forensic setting. However, results for both methods showed the same general trends.

For the second method, PCA was performed by eigenanalysis of the covariance matrix of a data set containing only the neat ignitable liquids. Then, scores for the burned carpet and ILRs were projected onto the principal components generated for the neat liquids. To calculate the projected score on each eigenvector, the data for the burned carpet and ILRs were mean-centered (relative to the mean of the neat ignitable liquid data set) and multiplied by the corresponding eigenvector. Projecting scores of the ILRs in this way ensured that discrimination among samples was based solely on differences among the ignitable liquids rather than differences introduced by the burning and extraction processes. Scores plots were generated in ORIGINPRO (version 7.5; OriginLab Corp., Northampton, MA), and loadings plots were generated in Microsoft Excel (Excel 2007; Microsoft Corp., Redmond, WA).

Results

Minimal Matrix Interferences

The TIC of the burned carpet contained mainly isoparaffinic (branched and unsaturated C_{11}–C_{12}) and alkane (C_{13}–C_{16}) components with some minor aromatic components (Fig. 1*A*). Chromatograms of spiked then burned samples (ILRs) were dominated by the presence of the ignitable liquid, as expected because of the high spike volume and light burning conditions. Despite the major contribution of the ignitable liquid to the ILR chromatogram, some chromatograms showed matrix interferences. For example, the chromatogram of the gasoline ILR showed a slight rise in the baseline around 10 min (Fig. 1*B*), which was consistent with isoparaffinic components from carpet (Fig. 1*A*).

The gasoline and diesel ILRs showed a relative decrease in the abundance of volatile aromatic components such as C_2- and C_3-alkylbenzenes when compared to the neat ignitable liquids (Fig. 1*B* compared to *C*). Chromatograms of ILRs of liquids without volatile aromatic components, such as torch fuel and paint thinner, or with a limited number of alkane or aromatic components, such as ultra pure paraffin lamp oil and adhesive remover, were very similar to their neat counterparts.

The first two principal components, based on PCA of the neat liquids, described 87.2% of the variance and no further appreciable discrimination was observed in retaining more principal components. Moreover, in examining higher principal components, artifacts, such as retention time misalignments, were identified as sources of variance, rather than differences among the set of neat ignitable liquids. The scores plot of principal component 1 (PC1) versus PC2 is shown in Fig. 2*A*, with the scores projected for the lightly burned carpet and ILRs with minimal matrix interferences. For ultra pure paraffin lamp oil, the neat liquid and the ILR were positioned negatively on both PC1 and PC2. Neat adhesive remover and the adhesive remover ILR were positioned positively on PC1 and negatively on PC2. The remaining four ignitable liquids, the corresponding ILRs, and the burned carpet (unspiked) were positioned around zero on PC1 and positively on PC2 (Fig. 2*B*). The PCA scores plot showed close association of replicates of all neat ignitable liquids and replicates of most ILRs (Fig. 2*A*). Spread was observed in the replicates of some ILRs (e.g., gasoline and adhesive remover ILRs), which may be attributed to variability in the burning and extraction processes. The position of samples in the scores plot can be further explained by interpreting the loadings plot to identify chemical components contributing most to the variance among samples.

The loadings plots of PC1 and PC2 are shown in Fig. 3. The first principal component discriminated the samples based on two groups of components: aromatics (ethylbenzene, *o*-xylene, and *p*-xylene) and normal alkanes (C_{12}–C_{14}) (Fig. 3*A*). The aromatic components loaded positively and the alkane components loaded negatively on PC1. Some minor C_3-alkylbenzenes were also shown to contribute positively to the variance, whereas minor isoparaffinic and naphthenic paraffinic components were shown to contribute negatively on the first principal component.

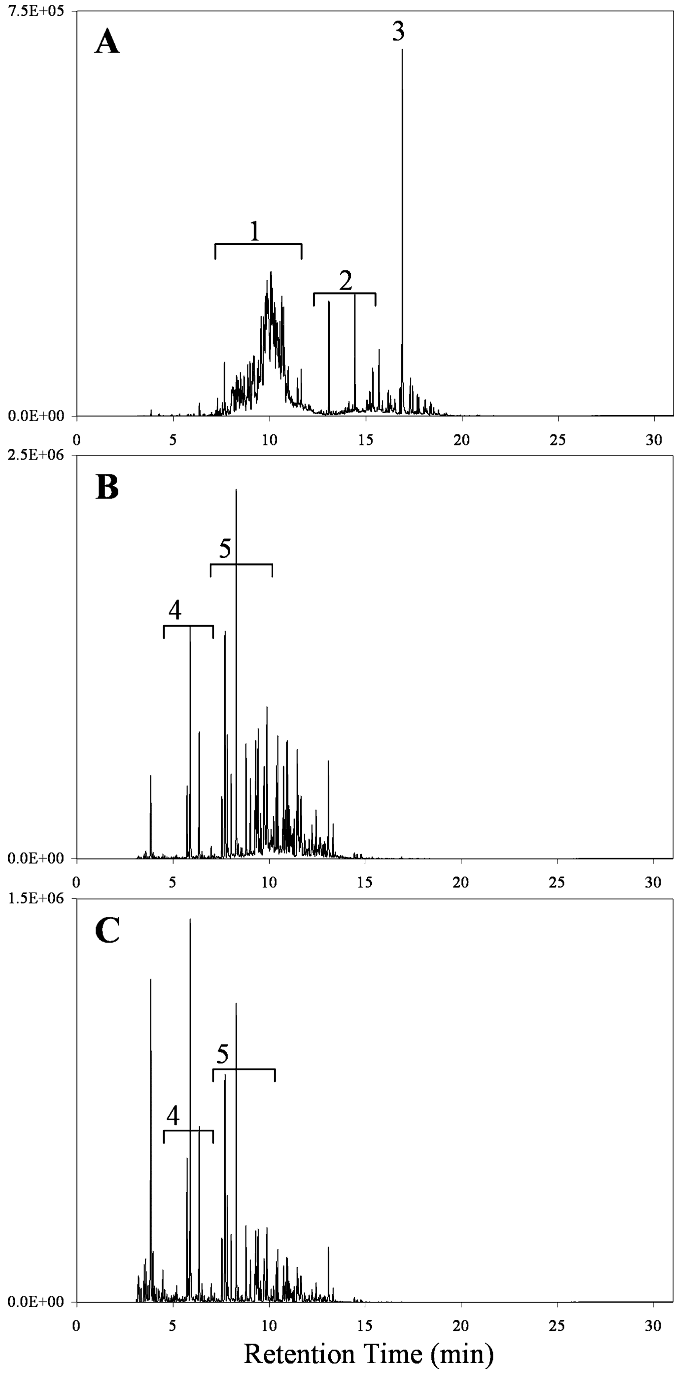

FIG. 1—*Chromatograms of (A) lightly burned carpet, (B) gasoline 1 spiked onto carpet then lightly burned, and (C) neat gasoline 1. Major components are labeled: (1)* C_{11}–C_{12} *isoparaffinic/naphthenic components, (2)* C_{13}, C_{14} *normal alkanes, (3) diester related to adipic acid, (4)* C_2*-alkylbenzenes, and (5)* C_3*-alkylbenzenes.*

The presence, absence, or relative ratio of the groups of components determined the position of the neat liquids on the first principal component in the scores plot. For example, adhesive remover and gasoline loaded positively on PC1 (Fig. 2). Adhesive remover contained only ethylbenzene, *o*-xylene, and *p*-xylene, which were the aromatic components contributing most to the variance described by PC1, whereas gasoline contained a higher content of the aromatic components than the alkane components. Ultra pure paraffin lamp oil, diesel, and torch fuel loaded negatively on PC1 (Fig. 2). Lamp oil contained only normal alkanes C_{12}–C_{14}, which were the alkane components contributing most to the variance described by PC1. Diesel contained a higher content of the alkane components than the aromatic components and torch fuel contained the alkane components as well as other minor isoparaffinic or naphthenic components that loaded negatively on PC1. Paint

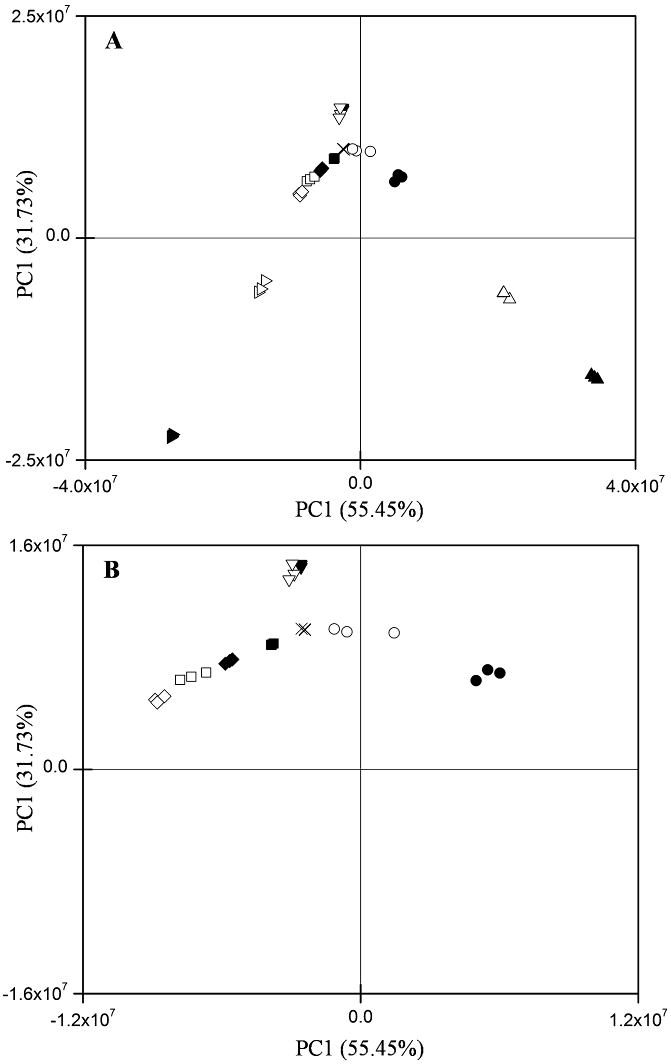

FIG. 2—*(A) Full view and (B) magnified view of the scores plot for six ignitable liquids and the corresponding ignitable liquid residues (ILRs) in the presence of minimal matrix interferences. Neat liquids are indicated by filled symbols, and ILRs are indicated by open symbols.* (■) *Diesel,* (●) *gasoline 1,* (▲) *adhesive remover,* (▶) *ultra pure paraffin lamp oil,* (▼) *paint thinner,* (◆) *torch fuel, (X) burned carpet (unspiked).*

thinner contained none of the major components identified in the loadings plot, but was positioned negatively on PC1 (Fig. 2) because it contained some of minor isoparaffinic or naphthenic components. The burned carpet, like torch fuel, contained normal alkanes (C_{13}–C_{14}) as well as other minor isoparaffinic or naphthenic components that caused it to load negatively on PC1.

The second principal component further discriminated the ignitable liquids based on isoparaffinic and naphthenic paraffinic content (Fig. 3*B*). Isoparaffinic and naphthenic paraffinic components loaded positively on PC2, whereas the C_2-alkylbenzenes and normal alkanes C_{12}–C_{14} identified on PC1 loaded negatively. As such, burned carpet and ignitable liquids that contained isoparaffinic or naphthenic paraffinic components (gasoline, diesel, paint thinner, and torch fuel) had positive scores on PC2 whereas liquids without those components (ultra pure paraffin lamp oil, adhesive remover) had negative scores on PC2.

The difference in positioning of the ILRs in the scores plot (Fig. 2) compared to the neat ignitable liquids was mainly caused by a loss of volatile aromatic components during the burning process. Paint thinner contained no volatile aromatic components so there was little visible difference between the chromatograms of the neat liquids and ILRs. As such, the ILR was closely associated with the neat ignitable liquid in the scores plot. The adhesive remover ILR shifted less positively on PC1 compared to the neat adhesive remover. This is consistent with a loss of the volatile aromatic components that loaded positively on PC1 relative to the neat liquid. The ultra pure paraffin lamp oil ILR shifted less negatively on PC1 compared to the neat lamp oil, indicating a decrease in abundance of the dominant alkane components in the loadings plot, relative to the neat liquid. The chromatograms of the adhesive remover and ultra pure paraffin lamp oil ILRs were very similar to the corresponding neat ignitable liquids, but contained minor naphthenic and isoparaffinic contributions from the burned carpet. As such, both the lamp oil ILR and the adhesive remover ILR shifted more positively on PC2. Despite the shift of the lamp oil ILR and adhesive remover ILR from the corresponding neat liquids, no other samples were positioned closely to either sample to complicate the association of the ILRs with the corresponding neat liquids in the scores plot. However, other ILRs were more difficult to associate with the corresponding neat liquids.

The gasoline ILR was positioned less positively on the first principal component than the neat gasoline, which is consistent with the loss of the aromatic components that loaded positively on the first principal component. The loss of aromatic components was observed in comparing the chromatograms of the gasoline ILR and neat gasoline (Fig. 1*B*,*C*). With the shift in the scores plot, the gasoline ILR was positioned closer to the diesel and burned carpet samples than to neat gasoline. This complicated the association of the gasoline ILR back to the neat gasoline based on the scores plot.

The diesel and torch fuel samples were positioned closely in the scores plot because of their similar chemical content. In comparing the chromatograms of neat diesel and torch fuel (Fig. 4), the samples contained many of the same naphthenic and isoparaffinic components. The main difference between the two neat liquids was a greater aromatic content in the neat diesel, which caused the neat diesel to be positioned more positively on PC1. As expected, the chromatogram of the diesel ILR showed a loss of aromatic components compared to the neat diesel, making the diesel ILR more similar to neat torch fuel than neat diesel. As such, the diesel ILR was positioned slightly more negatively on the first principal component than the neat diesel and close to neat torch fuel. With the positioning of the diesel and torch fuel samples, it was difficult to associate the ILR with the corresponding neat liquid based on the scores plot.

To further assess the association of an ILR with a neat ignitable liquid in the presence of matrix interferences, PPMC coefficients were also investigated. PPMC coefficients were useful in addition to PCA because PPMC coefficients use all variables in the chromatogram, whereas PCA uses only variables in the chromatograms that account for the greatest variance. The mean PPMC coefficients for replicates of the neat ignitable liquids ($n = 3$) and replicates of the ILRs ($n = 3$) are given in Table 2. The mean PPMC coefficients for replicates of neat ignitable liquids indicated a strong correlation (0.9871–0.9956), as expected. The mean PPMC coefficients for replicates of ILRs tended to be lower than the coefficients for replicates of the neat liquids; however, a strong correlation was still observed (0.8422–0.9930). The three samples with the lowest PPMC coefficients were adhesive remover ILR (0.8422 ± 0.1339), ultra pure paraffin lamp oil ILR (0.9285 ± 0.0353), and gasoline ILR (0.9585 ± 0.0219). Visual examination of the aligned ILR chromatograms showed that the

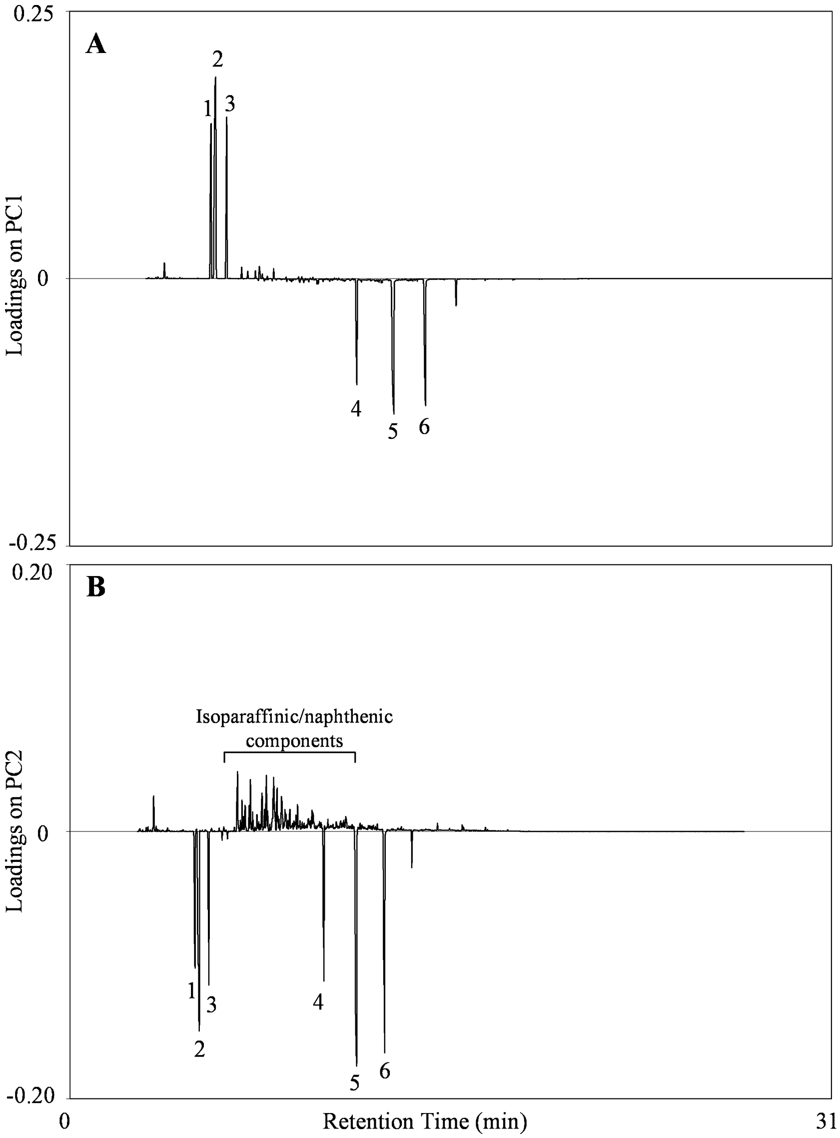

FIG. 3—*Loadings plots for (A) PC1 and (B) PC2 for six ignitable liquids and the corresponding ignitable liquid residues in the presence of minimal matrix interferences. Major components are labeled: (1) ethylbenzene, (2) o-xylene, (3) p-xylene, (4)* C_{12}*, (5)* C_{13}*, and (6)* C_{14}*.*

low PPMC coefficients were a result of variability in the burning process, as noted previously.

All correlation coefficients calculated between ILRs and corresponding neat liquids ($n = 9$) indicated a strong correlation (0.8704–0.9609), except gasoline that indicated a moderate correlation (0.7331 ± 0.0570) (Table 2). Because gasoline has a relatively high aromatic content, the chromatogram of the gasoline ILR was different than the neat ignitable liquid, causing a moderate correlation. Diesel, which showed a strong correlation with the diesel ILR (0.8704 ± 0.0070), was also affected by the loss of aromatic components, but not to the same degree as gasoline. Mean PPMC coefficients were highest for ignitable liquids with no volatile aromatic content to be lost in the burning process, such as torch fuel (0.9609 ± 0.0102) and ultra pure paraffin lamp oil (0.9468 ± 0.0446).

Correlation coefficients were not only calculated for replicates, but also calculated for all pair-wise comparisons of samples ($n = 9$, each liquid analyzed in triplicate). Neat paint thinner showed a weak to moderate degree of correlation with the burned carpet (0.4983 ± 0.0093) because of the similar isoparaffinic content in both samples. Neat diesel and neat torch fuel showed a moderate degree of correlation (0.5665 ± 0.0069) because both liquids contained similar chemical components, as noted previously. Because of the minimal change in the chromatograms of neat torch fuel and the torch fuel ILR (0.9609 ± 0.0102), a moderate correlation was also observed for diesel and the torch fuel ILR (0.5563 ± 0.0076). A higher correlation was observed between the diesel ILR and neat torch fuel (0.6698 ± 0.0187) as well as the diesel ILR and the torch fuel ILR (0.6886 ± 0.0184). This higher correlation was attributed to the loss of aromatic components in the diesel ILR compared to the neat diesel, making the diesel more similar to torch fuel.

The PPMC coefficients were useful to assess correlation among samples that were difficult to associate in the PCA scores plot. For example, the gasoline ILR was positioned close to burned carpet, paint thinner, and diesel in the scores plot, making it difficult to associate the gasoline ILR back to neat gasoline (Fig. 2). However, the mean PPMC coefficient for the gasoline ILR and the neat gasoline (0.7331 ± 0.0570) showed a moderate correlation, whereas PPMC coefficients for the gasoline ILR and all other samples showed a weak correlation with values below 0.5 (Table 3). The

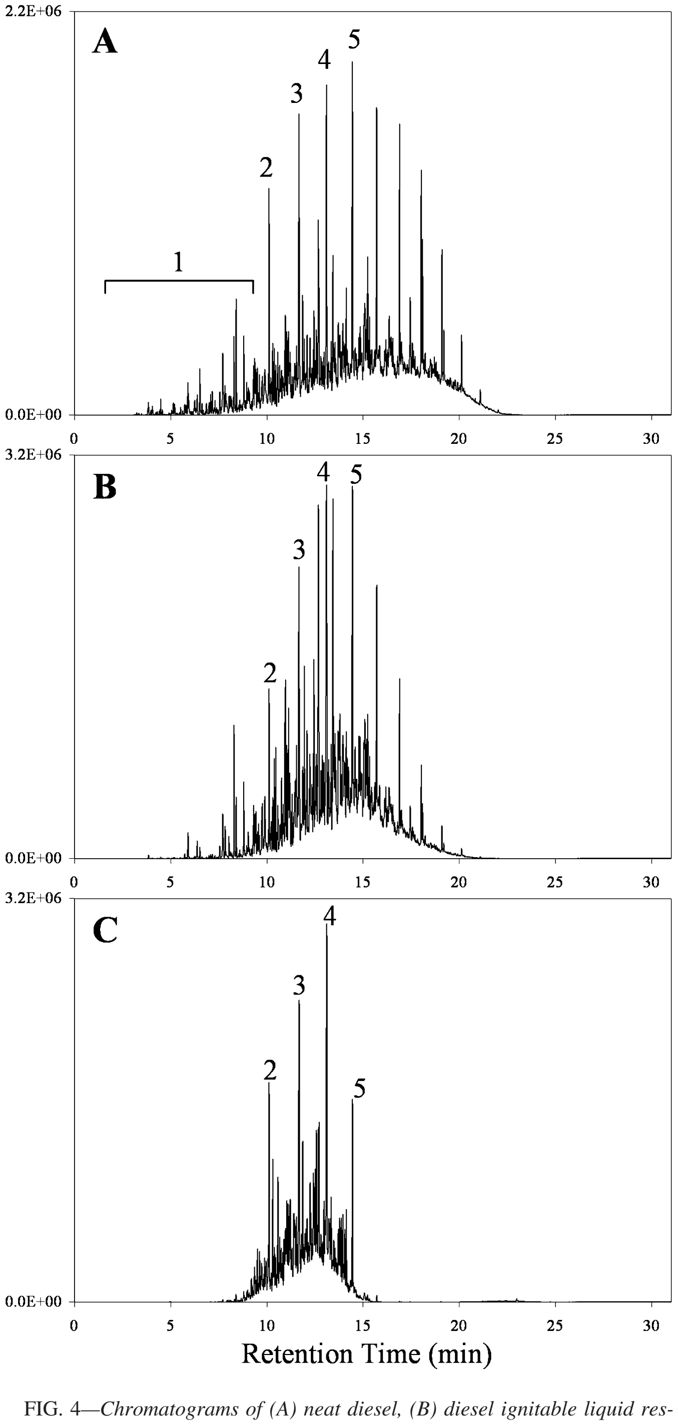

FIG. 4—*Chromatograms of (A) neat diesel, (B) diesel ignitable liquid residues, and (C) neat torch fuel, illustrating the similar chemical composition between the ignitable liquids. Major components are labeled: (1) aromatic components, (2)* C_{11}*, (3)* C_{12}*, (4)* C_{13}*, and (5)* C_{14}*.*

TABLE 2—*Mean Pearson product moment correlation coefficients ± SD for neat ignitable liquids replicates* (n = 3) *and ILR replicates* (n = 3) *as well as between neat ignitable liquid and the corresponding ILR* (n = 9) *in the presence of minimal matrix interferences.*

Ignitable Liquid	Neat	ILR	Neat versus ILR
Gasoline 1	0.9875 ± 0.0054	0.9585 ± 0.0219	0.7331 ± 0.0570
Diesel	0.9956 ± 0.0032	0.9930 ± 0.0020	0.8704 ± 0.0070
Adhesive remover	0.9897 ± 0.0082	0.8422 ± 0.1339	0.9088 ± 0.1143
Ultra pure paraffin lamp oil	0.9982 ± 0.0012	0.9285 ± 0.0353	0.9468 ± 0.0446
Paint thinner	0.9871 ± 0.0046	0.9882 ± 0.0029	0.8921 ± 0.0147
Torch fuel	0.9923 ± 0.0057	0.9907 ± 0.0011	0.9609 ± 0.0102

ILR, ignitable liquid residues.

TABLE 3—*Mean PPMC coefficients ± SD of samples that were difficult to discriminate based solely on the PC scores plot* (n = 9)*, in the presence of minimal matrix interferences.*

Comparison	Mean PPMC Coefficient	Degree of Correlation
Diesel versus gasoline 1 ILR	0.2323 ± 0.0287	Weak
Burned carpet versus gasoline 1 ILR	0.3463 ± 0.0123	Weak
Paint thinner versus gasoline 1 ILR	0.4065 ± 0.0163	Weak
Diesel versus torch fuel ILR	0.5563 ± 0.0076	Moderate
Diesel versus torch fuel	0.5665 ± 0.0069	Moderate
Torch fuel versus diesel ILR	0.6698 ± 0.0187	Moderate
Diesel ILR versus torch fuel ILR	0.6886 ± 0.0185	Moderate
Gasoline 1 versus gasoline 1 ILR	0.7331 ± 0.0570	Moderate
Diesel versus diesel ILR	0.8704 ± 0.0070	Strong
Torch fuel versus torch fuel ILR	0.9609 ± 0.0102	Strong

ILR, ignitable liquid residues; PPMC, Pearson product moment correlation.

diesel and torch fuel samples were also positioned closely in the scores plot and showed moderate correlations between the neat liquids and ILRs (Table 3). Nevertheless, the correlation coefficients were greatest between the ILRs and the corresponding neat liquid (Table 2), which allowed association.

Increased Matrix Interferences

The chromatogram of the heavily burned carpet showed different interferences than the lightly burned carpet (Fig. 1*A* compared to Fig. 5*A*). The TIC of the heavily burned carpet contained common interferences, such as styrene and benzaldehyde. These components were easily identified in the chromatogram of simulated ILRs (Fig. 5*B*). Interferences from the carpet complicated the chromatogram of several ILRs. For example, in the chromatogram of the gasoline ILR (Fig. 5*B*), styrene and benzaldehyde coeluted with C_2- and C_3-alkylbenzenes, making the chromatogram of the ILR different than that of the neat gasoline (Fig. 5*C*). However, ignitable liquids containing a complex mixture of components, such as diesel or torch fuel, masked the presence of many of the interfering components, even from the heavily burned carpet.

The scores plot of PC1 versus PC2 for the neat ignitable liquids is shown in Fig. 6. The scores for the heavily burned carpet and ILRs were projected on the same eigenvectors as the previous study to ensure that the ILRs were discriminated based on the same chemical variation among the neat liquids rather than differences in the burning conditions between the two studies. Close association was observed for replicates of most samples. Again, slight spread was observed for some ILRs because of the variability in burning. The projected positions of the ultra pure paraffin lamp oil ILR and the adhesive remover ILR with increased matrix interferences were similar to the projections of the corresponding ILRs with minimal matrix interferences. The ILRs for paint thinner, diesel, and torch fuel were positioned near the corresponding neat ignitable liquid. Compared to the ILRs with minimal matrix interferences, the ILRs with increased matrix interferences shifted closer to the unspiked, heavily burned carpet, which reflects the increased contribution of matrix interferences to the chromatograms of the ILRs.

Correlation coefficients of replicates of neat liquids and replicates of ILRs showed a high degree of correlation

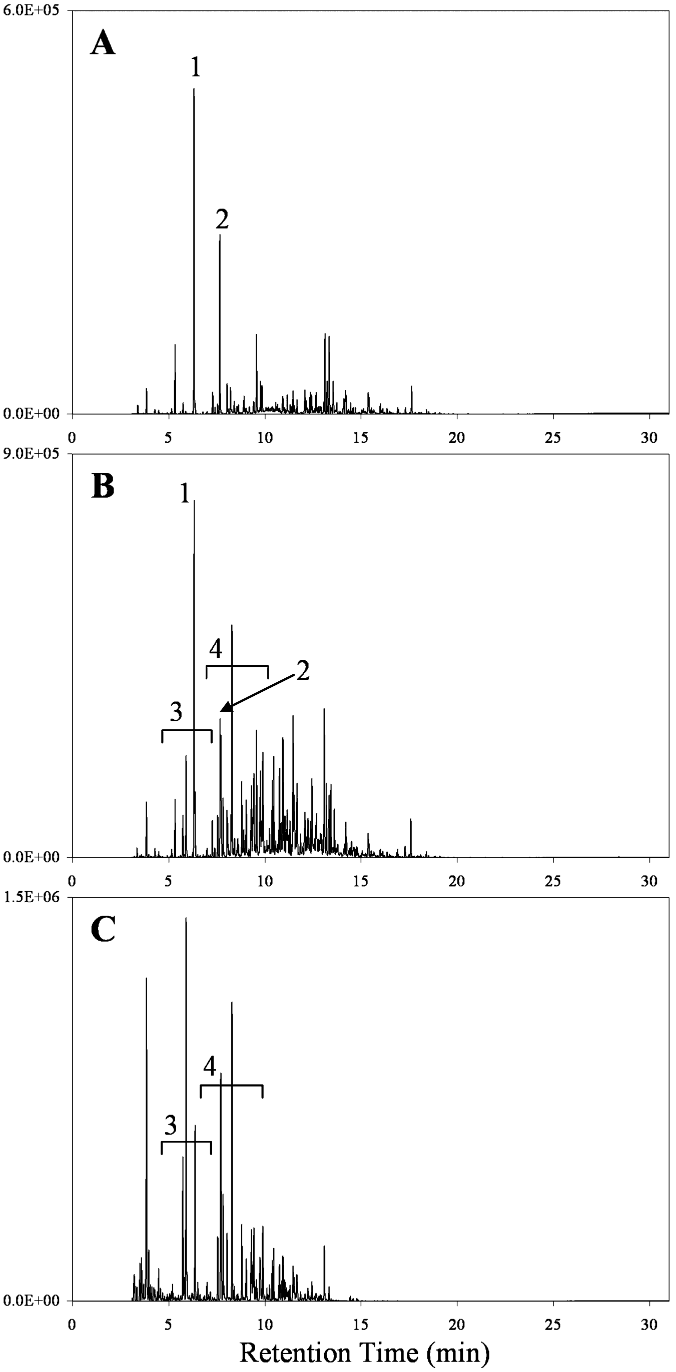

FIG. 5—*Chromatograms of (A) heavily burned carpet, (B) gasoline 1 spiked onto carpet then heavily burned, and (C) neat gasoline 1. Major components are labeled: (1) styrene, (2) benzaldehyde, (3) C_2-alkylbenzenes, and (4) C_3-alkylbenzenes.*

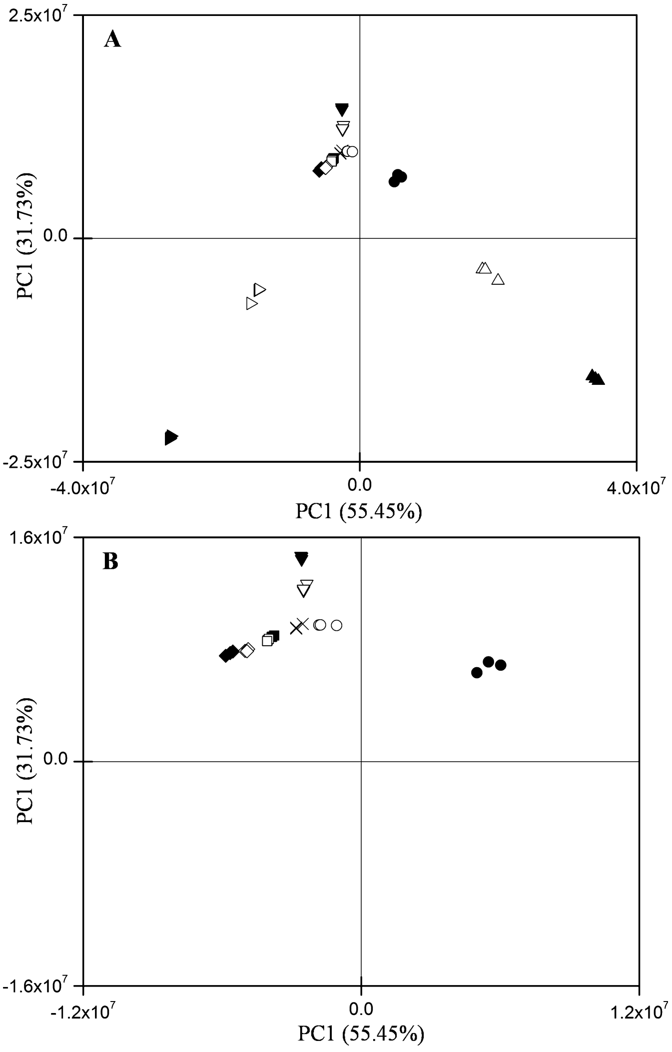

FIG. 6—*(A) Full view and (B) magnified view of scores plot for six ignitable liquids and the corresponding ignitable liquid residues (ILRs) in the presence of increased matrix interferences. Neat liquids are indicated by filled symbols, and ILRs are indicated by open symbols. (■) Diesel, (●) gasoline 1, (▲) adhesive remover, (▶) ultra pure paraffin lamp oil, (▼) paint thinner, (◆) torch fuel, (X) burned carpet (unspiked).*

TABLE 4—*Mean Pearson product moment correlation coefficients ± SD for neat ignitable liquid replicates (*n *= 3) and ILR replicates (*n *= 3) as well as between neat ignitable liquid and the corresponding ILR (*n *= 9) in the presence of increased matrix interferences.*

Ignitable Liquid	Neat	ILR	Neat versus ILR
Gasoline 1	0.9875 ± 0.0054	0.9641 ± 0.0169	0.5697 ± 0.0647
Diesel	0.9956 ± 0.0032	0.9932 ± 0.0036	0.9140 ± 0.0053
Adhesive remover	0.9897 ± 0.0082	0.9884 ± 0.0074	0.8022 ± 0.0241
Ultra pure paraffin lamp oil	0.9982 ± 0.0012	0.9693 ± 0.0136	0.8412 ± 0.0244
Paint thinner	0.9871 ± 0.0046	0.8807 ± 0.0730	0.7991 ± 0.0528
Torch fuel	0.9923 ± 0.0057	0.9840 ± 0.0106	0.9694 ± 0.0124

ILR, ignitable liquid residues.

(0.9871–0.9982 for neat replicates, 0.8807–0.9932 for ILR replicates) (Table 4). Lower PPMC coefficients were observed for the paint thinner ILR because of the variability in the burning process. The PPMC coefficients between ILRs and corresponding neat ignitable liquids also showed a moderate to strong degree of correlation (0.5697–0.9694) (Table 4). The gasoline ILR (0.5697 ± 0.0647) had the lowest average PPMC coefficient because of the high volatile aromatic content in gasoline that was most affected by burning. In addition, styrene and benzaldehyde from the carpet coeluted with *p*-xylene and 1-ethyl-3-methylbenzene, respectively, from the gasoline (Fig. 5*B*), which also contributed to lower PPMC coefficients. Neat ignitable liquids that had the strongest correlation with corresponding ILRs were those containing a complex mixture of components that masked many of the matrix interferences, such as diesel (0.9140 ± 0.0053) and torch fuel (0.9694 ± 0.0124). Compared to light burning conditions, ignitable liquids that contained few components, such as ultra pure paraffin lamp oil (0.8412 ± 0.0244) and adhesive remover (0.8022 ± 0.0241), showed lower mean PPMC coefficients because of an increased contribution of matrix interferences to the ILR chromatograms.

Again, PPMC coefficients were calculated for all samples ($n = 9$) and a moderate degree of correlation was observed between the following samples: neat diesel and neat torch fuel (0.5665 ± 0.0069), neat diesel and torch fuel ILR (0.5714 ± 0.0076), diesel ILR and neat torch fuel (0.6977 ± 0.0248), and diesel ILR and torch fuel ILR (0.7332 ± 0.0171). The diesel and torch fuel ILRs showed greater similarity compared to the lightly burned samples because of the addition of the same matrix interferences to the chromatogram of both ILRs.

A moderate degree of correlation was also observed between neat gasoline and the adhesive remover ILR (0.6174 ± 0.0107). However, in examining the PCA scores plot, these two samples were well separated in both PC1 and PC2. Comparison of the chromatograms indicated the presence of peaks at similar retention times, but with different abundances. This demonstrates the utility of PCA in discriminating samples that have similar components because PCA highlights the differences between the samples, whereas PPMC coefficients highlight the similarities.

Conversely, PPMC coefficients were useful in associating the gasoline ILR back to neat gasoline, which was difficult based solely on the PCA scores plot (Fig. 6). The mean correlation coefficient for the gasoline ILR and neat gasoline (0.5697 ± 0.0647) was much greater than the mean correlation coefficient calculated between the gasoline ILR and diesel (0.2452 ± 0.0249), paint thinner (0.3609 ± 0.0290), or burned carpet (0.4152 ± 0.0825), all of which indicated weak correlation.

The two previous examples illustrate the utility of using PCA and PPMC coefficients together. PCA is useful for associating and discriminating a large number of samples, whereas PPMC coefficients offer a pair-wise comparison that can be used to associate and discriminate individual samples. When used together, PPMC coefficients can support the association or discrimination of samples that are positioned closely in the scores plot. The two data analysis procedures are powerful when used together because the similarity among two chromatograms is assessed in PPMC coefficients, whereas only the variables that contribute most to the variance are considered in PCA.

Discrimination of ILRs from Additional Liquids in the Same ASTM Class

The previous study demonstrated the utility of PPMC coefficients and PCA to associate an ILR with a corresponding neat liquid in the presence of light and heavy burning conditions. However, it is also desirable to investigate the discrimination of the ILRs from other ignitable liquids in the same ASTM class. For this purpose, a new data set was compiled consisting of an additional six ignitable liquids (Table 1), one from each of the ASTM classes used previously, along with the original six liquids, six ILRs, and the burned carpet. It should be noted that a second lamp oil (Medallion) was added to the data set. This lamp oil was classed as a naphthenic paraffinic liquid, in contrast to the ultra pure paraffin lamp oil used in the original data set, which was classified as an alkane.

In examining the scores plot of PC1 versus PC2 (data not shown), the first two principal components account for 62.1% of the variance in the data set. The first principal component mainly discriminated lacquer thinner from the other liquids. From the loadings plots (data not shown), toluene loaded positively on PC1 whereas components, such as the C_2-alkylbenzenes and the normal alkanes C_{11}–C_{15}, loaded slightly negatively on PC1. As lacquer thinner contains only toluene, the liquid was positioned most positively on PC1 whereas the remaining liquids were positioned negatively on PC1 but close to zero. Although PC1 accounts for the greatest variance (41.6%), it provides little discrimination of the neat ignitable liquids. Consequently, the following discussion will focus on PC2 and PC3, which offered greater discrimination.

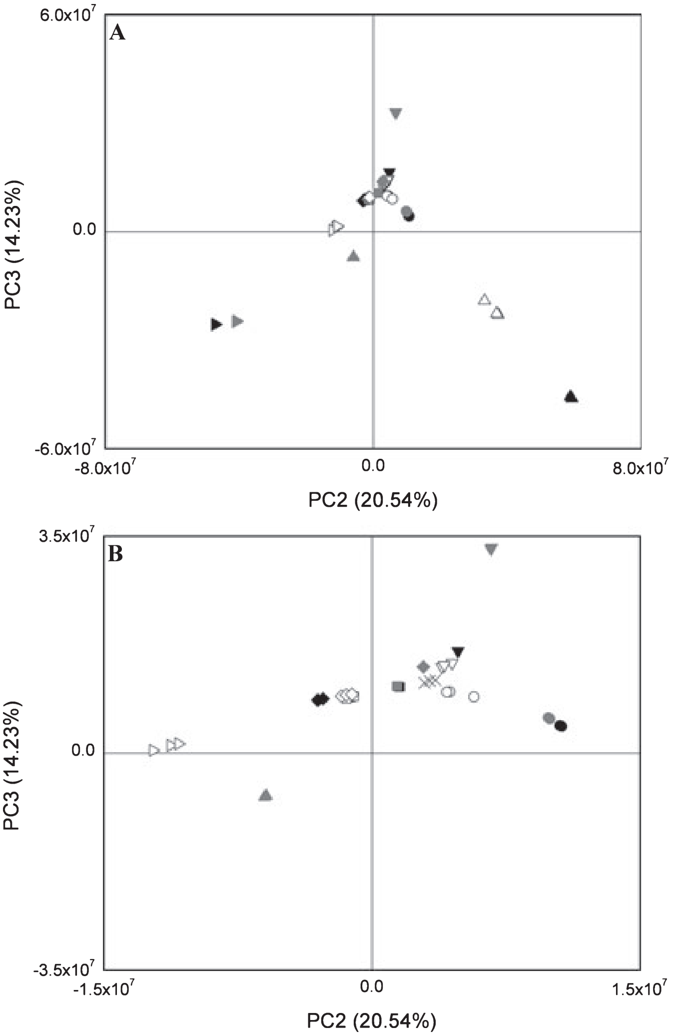

FIG. 7—*(A) Full view and (B) magnified view of scores plot for 12 ignitable liquids and six ignitable liquid residues (ILRs) in the presence of increased matrix interferences. Neat liquids are indicated by filled symbols, and ILRs are indicated by open symbols. (■) Diesel, (■) kerosene, (●) gasoline 1, (●) gasoline 2, (▲) adhesive remover, (▲) lacquer thinner, (▶) ultra pure paraffin lamp oil, (▶) candle wax lifter, (▼) paint thinner, (▼) fabric protector, (◆) torch fuel, (◆) lamp oil, (X) burned carpet (unspiked).*

The scores plot of PC2 versus PC3 is shown in Fig. 7, with scores projected for the heavily burned carpet and ILRs. The third PC accounts for an additional 14.2% of the variance in the data set. Compared to the scores plot for PC1 versus PC2 for the original six ignitable liquids (Fig. 6), it can be seen that the original liquids have similar relative positions. In examining the loadings plots

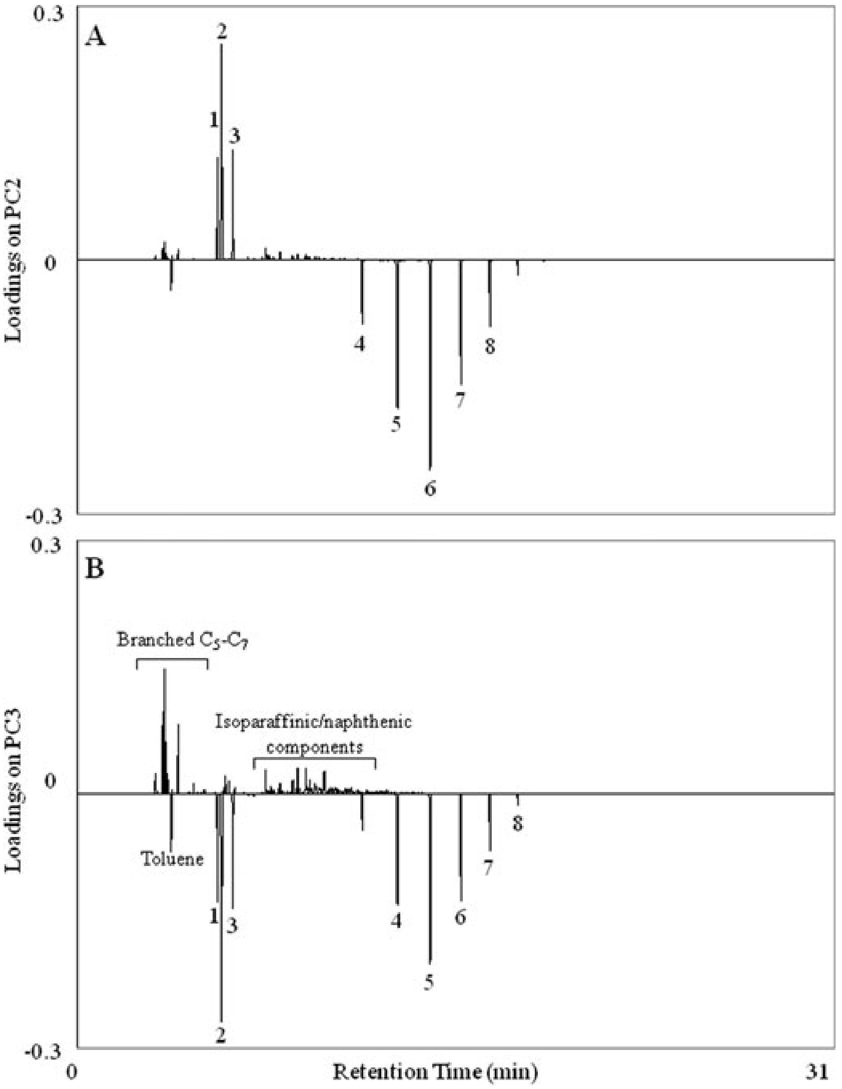

FIG. 8—*Loadings plots for (A) PC2 and (B) PC3 for 12 ignitable liquids and six ignitable liquid residues in the presence of increased matrix interferences. Major components are labeled: (1) ethylbenzene, (2) o-*xylene, (3) *p-xylene, (4)* C_{12}, *(5)* C_{13}, *(6)* C_{14}, *(7)* C_{15}, *and (8)* C_{16}.

for the larger data set (Fig. 8), PC2 and PC3 were similar to PC1 and PC2, respectively, for the data set containing the original six liquids (Fig. 3). However, because of the greater number of liquids with varying chemical composition in the larger data set, additional isoparaffinic components (branched C_5–C_7), toluene, and normal alkanes (C_{15}–C_{17}) contributed to the variance and were identified in PC2 and PC3.

For most liquid classes, the two ignitable liquids from the same class were positioned closely in the scores plot because of their similar chemical composition (Fig. 7). However, not all liquids within the same class have such similar chemical composition. For example, lacquer thinner and adhesive remover are both in the aromatic class yet lacquer thinner contains only toluene whereas adhesive remover contains only C_2-alkylbenzenes. As a result of this difference in chemical composition, the two aromatic liquids were not positioned closely in the scores plot. Similarly, as the isoparaffinic liquids (paint thinner and fabric protector) differ in the range of branched alkanes (Table 1), the two liquids were not positioned closely in the scores plot.

In some cases, positioning on the scores plot could be used to associate the ILR with the corresponding neat liquid. For example, in the aromatic class, the adhesive remover ILR was positioned between adhesive remover and lacquer thinner. Because of the difference in chemical composition, lacquer thinner was positioned negatively on both PC2 and PC3 whereas adhesive remover and the adhesive remover ILR were positioned positively on PC2 and negatively on PC3. Mean PPMC coefficients between the adhesive remover ILR and each neat liquid were also calculated to confirm the association. The mean PPMC coefficient between the adhesive remover ILR and neat adhesive remover indicated a strong correlation (0.8195 ± 0.0193), whereas the mean PPMC coefficient between the adhesive remover ILR and lacquer thinner showed no correlation (0.0038 ± 0.0004). However, positioning on the scores plot alone was often not sufficient to associate the ILR with the neat liquid, because of the additional liquids present. In such cases, PPMC coefficients were necessary to assess the similarity among closely positioned liquids and ILRs.

In the isoparaffinic class, the paint thinner ILR was positioned close to the neat liquid and separate from the fabric protector. However, the paint thinner ILR was also closely positioned to the burned carpet, as well as a naphthenic paraffinic liquid (lamp oil) and the gasoline ILR. Based on PPMC coefficients, there was a moderate correlation between the paint thinner ILR and neat paint thinner (0.7389 ± 0.0629) but only a weak correlation between the paint thinner ILR and burned carpet (0.1902 ± 0.0881), lamp oil (0.3115 ± 0.0339), and the gasoline ILR (0.4010 ± 0.0651). Similarly, the torch fuel ILR was positioned close to neat torch fuel but overlapped with the diesel ILR. The PPMC coefficients indicated a strong correlation between the torch fuel ILR and neat torch fuel (0.8606 ± 0.0138) but only a moderate correlation between the torch fuel ILR and the diesel ILR (0.7332 ± 0.0171).

The ultra pure paraffin lamp oil ILR was more affected by the presence of the second liquid from the alkane class. The neat liquids (ultra pure paraffin lamp oil and candle wax lifter) were negative on PC2 and PC3, whereas the ultra pure paraffin lamp oil ILR was positioned close to zero on both PCs. The neat liquids contained normal alkanes, which load negatively on PC2 and PC3. However, in the ultra pure paraffin lamp oil ILR, the abundance of the normal alkanes was significantly less and hence the ILR was positioned closer to zero. As a result, the ILR was positioned more closely to neat lacquer thinner and neat torch fuel, which are members of the aromatic and naphthenic paraffinic classes, respectively. The mean PPMC coefficient between the ultra pure paraffin lamp oil ILR and neat lamp oil showed a weak correlation (0.4457 ± 0.0128), potentially owing to the significant difference in relative abundance of components in the ILR and neat liquid. Nonetheless, there was less correlation between the ultra pure paraffin lamp oil ILR and candle wax lifter (0.2388 ± 0.0048) and the ultra pure paraffin lamp oil ILR and torch fuel (0.3319 ± 0.0084). There was no correlation between the ILR and lacquer thinner (−0.0044 ± 0.0001). Thus, despite a weak correlation, association of the ultra pure paraffin lamp oil ILR and the corresponding neat liquid was still possible.

ILRs from the gasoline and petroleum distillate classes were more difficult to associate with the corresponding neat liquids. In the scores plot, the gasoline ILR was positioned more closely to the burned carpet, neat lamp oil (naphthenic paraffinic), neat paint thinner, and the paint thinner ILR than to either of the two gasoline samples in the data set. However, PPMC coefficients indicated only a weak correlation between the gasoline ILR and carpet (0.4152 ± 0.0825), neat lamp oil (0.2330 ± 0.0008), neat paint thinner (0.2665 ± 0.0225), and the paint thinner ILR (0.4152 ± 0.0825). A moderate correlation was determined between the gasoline ILR and both neat gasoline samples (0.5948 ± 0.0589 for gasoline 1 and 0.5904 ± 0.0631 for gasoline 2). As a result, the gasoline ILR could not be unambiguously associated with the corresponding neat liquid but could be associated with the class of liquid. This apparent deficiency is expected, because of the similarity in chemical composition between the two neat gasoline samples.

Similarly, the two liquids in the petroleum distillate class (diesel and kerosene) have similar chemical composition, particularly those components that are contributing to the variance in PC2 and PC3 (as identified from the loadings plots). Consequently, neat diesel and neat kerosene overlapped in the scores plot. The diesel ILR overlapped with the torch fuel ILR and was positioned more closely to neat torch fuel than either of the neat petroleum distillates. The mean PPMC coefficients indicate a moderate correlation between the diesel ILR and both the torch fuel ILR (0.7332 ± 0.0171) and the neat torch fuel (0.6342 ± 0.0203). There is a strong correlation between the diesel ILR and neat diesel (0.8275 ± 0.0062) and neat kerosene (0.8579 ± 0.0223). As with the gasoline class, the diesel ILR cannot be associated with the corresponding neat liquid, but can be associated with the class of liquid.

Discussion

By using PPMC coefficients in conjunction with PCA, each ILR was associated with the neat ignitable liquid and discriminated from matrix interferences under both light and heavy burning conditions. With heavy burning, ILRs showed a greater loss of aromatic components compared to light burning. However, the increased weathering of the ignitable liquids with heavy burning had a minimal effect on the successful association of the ILR with the neat liquid. Based on the position of the samples in the scores plot for both light and heavy burning (Figs 2 and 6), most ILRs were successfully associated with the neat liquid using only PCA. However, because of the positioning of the gasoline ILR, diesel ILR, and torch fuel ILR, the use of PPMC coefficients as well as PCA was required to associate each ILR back to the corresponding neat liquid.

Successful discrimination from matrix interferences was achieved regardless of the extent of burning. With light burning, isoparaffinic and naphthenic components from the carpet were prevalent, but were generally masked by the components from the ignitable liquid because of the high spike volume. With heavy burning, more abundant matrix interferences from burning were observed, such as styrene and benzaldehyde. Several components from the burned carpet coeluted with components in the ignitable liquids, making the chromatogram of the ILR visually different from that of the neat liquid. The utility of the method was tested by introducing additional liquids into the data set. Most ILRs could still be associated with the corresponding neat liquid, using both PCA and PPMC coefficients. However, for the petroleum distillates and gasoline classes, only the class of the ILR could be determined, because of the similarity in chemical composition of liquids within these two classes.

The results from the studies reported herein demonstrate that the combination of PCA and PPMC coefficients may be useful for overcoming the two main problems associated with visual assessment of ILR chromatograms: weathering of the ignitable liquid and matrix interferences. Using PCA and PPMC coefficients, the class of ILR can be identified and, depending on the similarity in chemical composition of liquids in the same class, the ILR can be associated with the corresponding neat liquid. Further studies are currently under way to examine additional ignitable liquids and matrices with different interferences and to assess the subsequent ability to associate the ILR with the neat liquid or class of liquid.

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