

PAPER**CRIMINALISTICS**

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Effect of Substrate Interferences from High-Density Polyethylene on Association of Simulated Ignitable Liquid Residues with the Corresponding Liquid

ABSTRACT: The effect of substrate interferences from high-density polyethylene (HDPE) on the ability to associate an ignitable liquid residue with the corresponding liquid standard, using statistical procedures, is demonstrated. Gasoline, kerosene, and lighter fluid, at three different evaporation levels, were spiked onto HDPE and subsequently burned to generate simulated ignitable liquid residues (ILRs). Samples were extracted using a passive headspace procedure and analyzed by gas chromatography–mass spectrometry. The total ion chromatograms were subjected to data pretreatment procedures prior to principal components analysis and Pearson product moment correlation. Using the combination of these statistical procedures, simulated ILRs were successfully associated with the corresponding liquid type, despite the presence of compounds inherent to the HDPE substrate, as well as those resulting from pyrolysis of the substrate.

KEYWORDS: forensic science, simulated ignitable liquid residues, gas chromatography–mass spectrometry, high-density polyethylene, substrate interferences, multivariate statistical analysis, Pearson product moment correlation, principal components analysis

Fire debris analysis is often recognized as one of the most difficult forensic disciplines (1). Identification of an ignitable liquid residue (ILR) is currently based on a visual comparison of the chromatogram obtained from the debris and those of known ignitable liquids. The comparisons are based not only on the total ion chromatogram, but also on extracted ion chromatograms or extracted ion profiles of characteristic compound classes. However, comparisons with reference chromatograms are complicated by evaporation of the ignitable liquid, the presence of interferences inherent to the substrate, and the introduction of additional interferences due to thermal degradation and/or pyrolysis of the substrate.

Numerous researchers have specifically investigated the inherent compounds and pyrolysis products from a variety of common substrates (1–4). Lentini et al. (2) analyzed volatile compounds extracted from numerous unburned household substrates, including newspapers and magazines, as well as clothing and shoes. Many of the target compounds commonly used for ignitable liquid identification were inherently present in these substrates. For example, toluene and xylenes, which are used for the identification of gasoline, were identified in adhesives, shoes,

clothing, and other substrates containing polymers. The authors advocated the use of comparison samples whenever possible to prevent false-positive identification of ignitable liquids in such substrates.

A further study by Almirall and Furton also identified inherent interferences and pyrolysis products in a variety of other household substrates (3). Various types of carpet, along with synthetic flooring and plastic items, such as bottles, cutlery, and bags, were investigated. Many target compounds used for ignitable liquid identification were found in the pyrolyzed substrates, for example, normal and branched alkanes, as well as aromatic products such as 2-methylnaphthalene. However, the relative concentrations of these compounds in the substrates were sufficiently different from those expected in the ignitable liquids that distinction of the substrate and liquid was possible.

Focusing on plastic substrates, Stauffer described mechanisms through which polymers degrade under pyrolysis conditions (1). For example, polyethylene undergoes a random scission process in which the carbon–carbon bonds in the backbone of the polymer break at random sites, resulting in the formation of alkadienes, alkenes, and alkanes. In the resulting total ion chromatogram, the pyrolysis of polyethylene is indicated by triplets of peaks for each carbon number, which correspond to the alkadiene, the alkene, and the alkane. In another study, Ballice focused on compounds generated during pyrolysis of polypropylene (4). For this polymer, compounds ranging in carbon number from 1 to 26 were identified, with the major compounds being branched C₉ compounds such as 2-methyl-4-octene and 2,6-dimethyl-2,4-heptadiene.

Keto demonstrated the use of extracted ion chromatograms and target compound analysis to identify petroleum distillates

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even in the presence of pyrolysis products (5). Pyrolysis of polyethylene resulted in the characteristic pattern of n-alkanes similar to that observed in kerosene. However, chromatograms of the pyrolyzed substrate and kerosene could be distinguished based on alkenes, which were present only in the substrate, and branched alkanes, which were present only in the liquid. Extracted ion chromatograms (EICs) of m/z 83 were also used for further distinction. This m/z value represented the alkenes in the pyrolyzed polyethylene and the alkylcyclohexanes in kerosene. However, the retention times of these two compound classes were sufficiently different to allow distinction.

Lentini also demonstrated the use of EICs in fire debris analysis, in this case to distinguish smoke condensate of polyethylene from weathered diesel (6). Using m/z 55 and m/z 57 and focusing on the C_{16} - C_{18} region of the chromatograms, EICs of diesel were dominated by the normal alkanes, with pristane and phytane also present at significant abundance. In comparison, the corresponding EICs for the polyethylene smoke condensate were dominated by the alkenes, with no significant contribution from pristane and phytane. Moreover, the alkadienes were readily apparent in the EIC of m/z 57, enabling further distinction of polyethylene from diesel.

To enhance practicality in forensic laboratories, the effect of compounds inherent to the substrate and those introduced as a result of pyrolysis on the identification of ignitable liquid residues must be further investigated. The potential of multivariate statistical procedures for association and classification of ignitable liquids has already been demonstrated (7–11). The use of more objective statistical procedures is also in accordance with the 2009 National Academy of Sciences' National Research Council report, "Strengthening Forensic Science in the United States: A Path Forward," which advocated greater use of statistical procedures for forensic evidence comparisons (12).

However, these statistical procedures must be further investigated for utility in identifying an ignitable liquid residue in the presence of evaporation, substrate interferences, and pyrolysis products. Tan et al. (13) prepared simulated ILRs, which consisted of one liquid from each of five classes defined by ASTM International spiked onto polyolefin-piled carpet that was subsequently ignited. Liquid residues extracted from the burned substrate were analyzed by gas chromatography–mass spectrometry (GC-MS), and the resulting chromatogram was divided into 19 equal time segments. The abundance within each segment was summed, and the 19 summed abundances were used as variables for data analysis. Using a soft independent modeling of class analogy (SIMCA) approach, all liquid residues extracted from the burned substrate were correctly classified. However, the authors neither identified the substrate interferences nor indicated the extent of the interferences.

Baerncopf et al. (14) used principal components analysis (PCA) in combination with Pearson product moment correlation (PPMC) to investigate association of simulated ILRs with the corresponding neat liquid. Liquids (one from each of six ASTM classes) were spiked onto nylon carpet that was subsequently burned, extracted, and analyzed by GC-MS. In this study, the full total ion chromatogram, rather than selected regions or target compounds, was used for data analysis. While successful association was demonstrated, the volume of liquid spiked onto the substrate was relatively high. As a result, the liquid dominated the chromatogram, with only minimal contributions from compounds in the substrate.

The purpose of the study reported herein was to further investigate the effects of substrate interferences on the association of

simulated ILRs with the corresponding liquid. For this proof-of-concept study, high-density polyethylene (HDPE) was used as the substrate, and three liquids were investigated: gasoline, kerosene, and lighter fluid. These liquids were chosen due to their wide availability, common use, and chemical complexity. Each liquid was evaporated to three different levels by volume and spiked onto individual samples of HDPE that were then burned for a specified time. As noted by Stauffer, thermal degradation typically occurs at temperatures ranging from 100 to 300°C, while pyrolysis occurs at temperatures greater than 300°C (1). Although a propane torch was used for burning, the temperature of the substrate surface was not determined, and hence, in this initial study, the effects of thermal degradation and/or pyrolysis are demonstrated. The simulated ILRs were extracted and analyzed by GC-MS, and the resulting total ion chromatograms were subjected to various pretreatment procedures prior to data analysis. Principal components analysis and PPMC were used to assess association of the simulated ILRs with the corresponding liquid, despite evaporation, substrate interferences, and thermal degradation and/or pyrolysis.

Materials and Methods

Preparation of Liquid Standards

Gasoline and kerosene were purchased from local gas stations, while lighter fluid was purchased from a local grocery store in the East Lansing, MI area. Aliquots of each liquid were evaporated under a stream of purified air. Gasoline and lighter fluid were evaporated to reduce the original volume by 10% and by 90%, while kerosene was evaporated to reduce the original volume by 10% and by 70%. The neat and evaporated liquids were diluted 1:25 (v/v) in dichloromethane (Spectrograde, Jade Scientific, Canton, MI) that contained 0.03 M nitrobenzene (Mallinckrodt, Paris, KY) as an internal standard. All liquids were stored in acid-washed amber bottles in the refrigerator until analysis.

Replicates ($n = 5$) of each liquid standard were spiked (20 μ L) onto separate pieces of Kimwipe™, each of which was placed in a separate nylon bag (Grand River Products LLC, Grosse Pointe Farms, MI), into which an activated carbon strip (2.5 \times 5 mm, Albrayco Laboratories, Inc., Cromwell, CT) was also suspended using a paper clip that had been prerinsed in dichloromethane. Bags were then sealed with general purpose masking tape (Duck Products, Avon, OH) and placed in an oven at 80°C for 4 h, in accordance with procedures recommended by ASTM International (15). Following extraction, the carbon strip was eluted with 200 μ L dichloromethane containing nitrobenzene, and the extract was analyzed by GC-MS.

A mixed standard, containing all ignitable liquids, was necessary for retention time alignment. This standard was prepared by diluting neat gasoline, neat kerosene, and neat lighter fluid 1:25 (v/v) in the same aliquot of dichloromethane. The mixed standard was then spiked onto a single Kimwipe™ in a nylon bag. The standard was extracted as described above and analyzed by GC-MS.

Investigation of Inherent Substrate Interference Effects in High-Density Polyethylene

High-density polyethylene samples were obtained from recycled solvent bottles. Samples consisted of the plastic from (i) the sides of the bottle (total of eight 4 cm \times 4 cm squares), (ii) half of the bottom of the bottle, cut into 4 cm \times 4 cm squares, or

(iii) half of the top of the bottle, excluding the handle, cut into 4 cm × 4 cm squares.

To investigate the burn time that generated abundant interference compounds, samples of HDPE were burned using a propane torch for times ranging from 0 to 120 s. After the appropriate burn time, samples were smothered with an overturned beaker and placed in separate nylon bags containing activated carbon strips. The samples were extracted for four hours at 80°C, the carbon strip was eluted with 200 µL dichloromethane containing nitrobenzene, and the extract was analyzed by GC-MS.

Preparation of Simulated ILRs

Separate samples of HDPE were spiked with each of the liquid standards ($n = 5$ for each standard) and then burned for 60 s to generate significant substrate interferences. Spike volumes varied by liquid as follows: 350 µL for gasoline, 200 µL for lighter fluid, and 175 µL for kerosene. These volumes were chosen such that the ignitable liquid did not mask the interferences from the substrate in the subsequent chromatogram. In addition, five samples of HDPE were burned for 60 s with no ignitable liquid added, to serve as control samples. All samples were placed in separate nylon bags and then extracted as described previously and analyzed by GC-MS.

GC-MS Analysis of Liquids and Simulated ILRs

All extracts were analyzed using an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a DB-5 ms column (0.25 mm × 30 m × 0.25 µm, Agilent Technologies, Palo Alto, CA) and an Agilent 7683B series automatic liquid sampler. Ultra-high-purity helium was used as the carrier gas with a nominal flow rate of 1 mL/min. The inlet was maintained at 250°C, and 1 µL of extract was injected in pulsed splitless mode, using a pulse of 15 psi for 0.25 min. The oven temperature program was based on the program used by the National Center for Forensic Science: 40°C for 3 min, 10°C/min to 280°C, with a final hold of 4 min (16). The transfer line to the Agilent 5975 mass selective detector (Agilent Technologies) was maintained at 280°C. Electron ionization (70 eV) was used, and the quadrupole mass analyzer was operated in the full-scan mode (m/z 50–550) with a scan rate of 2.91 scans/s. All extracts were analyzed in triplicate.

Data Pretreatment and Analysis

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

Prior to data analysis, the TICs were subjected to several preprocessing steps to minimize nonchemical sources of variance. The first step involved removing the caprolactam peak in each TIC using the background subtraction function in the ChemStation software. Because caprolactam is a component of the nylon bags, background subtraction was necessary to remove the irreproducible contribution that would otherwise introduce variance into the data set. Each TIC was then smoothed using the Savitzky–Golay algorithm available in the ChemStation software.

Total ion chromatograms in each data set were retention time-aligned using a correlation optimized warping algorithm (LineUp 3.0, Infometrix, Bothell, WA) with a warp of 2 data points and a segment size of 75 data points. The TICs were then normalized in two stages: first to the internal standard, followed by a total area normalization of each set of replicates. To do this, the abundance at each retention time was initially divided by the abundance of the internal standard in the TIC. Then, the area of each TIC in a set of replicate extracts (e.g., all replicates of neat gasoline) was summed, and the average area was calculated. The abundance at each retention time was divided by the area of that TIC and multiplied by the average area of all replicate TICs ($n = 15$ for triplicate analysis of five extractions of each liquid). All normalization calculations were performed in Microsoft Excel (Microsoft Corp., Redmond, WA).

Total ion chromatograms of only the liquid standards were subjected to PCA using MATLAB (version R2010b, The Mathworks, Natick, MA). The eigenvectors and eigenvalues were then used to generate scores and loadings plots in Microsoft Excel. Data for the simulated ILRs were mean-centered to the liquid standards and then multiplied by the eigenvector for PC1. This product was summed for each simulated ILR to generate the score on PC1 for that ILR. The procedure was repeated, multiplying the mean-centered data by the eigenvector for PC2 and summing, to generate the score on PC2 for each ILR. The scores for the ILRs were then projected onto the scores plot generated for the liquid standards. Projecting scores in this way ensures that similarities and differences between the liquid standards and extracts are chemical in nature, rather than artifacts of the burning, extraction, and analysis procedures.

Pearson product moment correlation (PPMC) coefficients were also calculated pairwise for all TICs in each data set (i.e., liquid standards alone and liquid standards plus simulated ILRs), using Microsoft Excel. Coefficients range from +1 to -1, with the sign indicating positive or negative correlation (17). Coefficients in the range of ±0.8–1.0 indicate strong correlation between samples, coefficients in the range of ±0.50–0.79 indicate moderate correlation, coefficients <0.50 indicate weak correlation, and coefficients close to zero indicate no correlation (17). Because PPMC coefficients are a measure of similarity, the coefficients can be considered complementary to PCA, which highlights the differences among samples. Hence, PPMC coefficients were used to assess precision in the extraction and analysis procedures, as well as similarity between the simulated ILRs and corresponding liquid standards.

Results

Assessment of Precision in the Extraction and Analysis Procedures

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 ($r > 0.988$) between 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 \pm 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

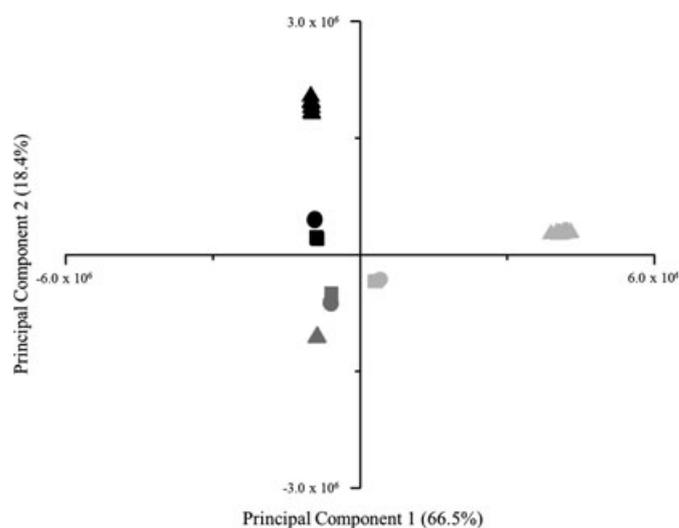


FIG. 1—Scores plot of principal component 1 vs. principal component 2 based on total ion chromatograms for the ignitable liquid standards ($n = 15$ for each standard). Gasoline is shown in black; kerosene, in dark gray; and lighter fluid, in light gray. Symbols denote the level of evaporation as follows: 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.

Association and Discrimination of Gasoline, Kerosene, and Lighter Fluid Standards using PCA

The scores plot of the first two principal components (PC1 and PC2, respectively) for the liquid standards accounts for 84.9% of the total variance in the data set (Fig. 1). The gasoline standards are positioned negatively on PC1 and positively on PC2, while the kerosene standards are positioned negatively on both PCs in the scores plot. The lighter fluid standards are positioned positively on PC1, but the neat and 10% evaporated standards are positioned negatively on PC2, while the 90% evaporated standard is positioned positively. The positioning of all standards can be explained with reference to the loadings plots (Fig. 2).

On PC1, the normal alkanes C_9 – C_{11} are weighted positively, while toluene, C_2 -alkylbenzenes, 1,3,5-trimethylbenzene (a C_3 -alkylbenzene), and the normal alkanes C_{13} – C_{16} are weighted negatively (Fig. 2A). On PC2, toluene, the C_2 -alkylbenzenes, C_3 -alkylbenzenes, C_4 -alkylbenzenes, and C_{10} are weighted positively, while the normal alkanes C_9 and C_{12} – C_{16} are weighted negatively (Fig. 2B).

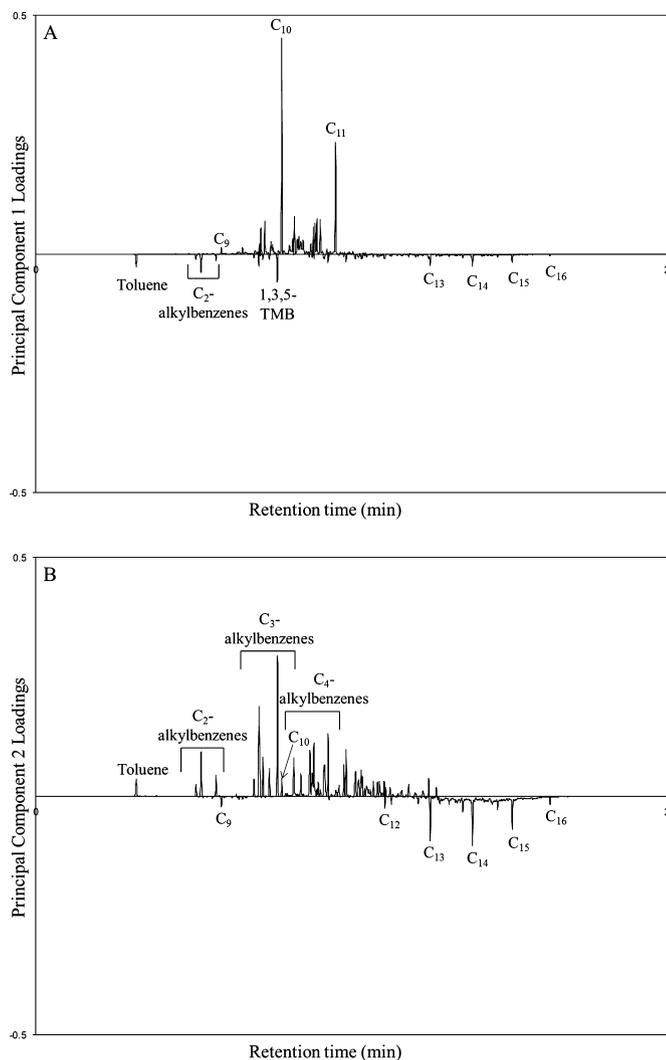


FIG. 2—Loadings plot for (A) principal component 1 and (B) principal component 2 based on the total ion chromatograms for the neat and evaporated liquid standards.

Toluene, C_2 -alkylbenzenes, and C_3 -alkylbenzenes are characteristic compounds in gasoline. Because these compounds have a negative contribution to PC1, the gasoline standards are positioned negatively on PC1 in the scores plot. These same compounds, in addition to the C_4 -alkylbenzenes, also have a positive contribution to PC2, resulting in the gasoline standards having a positive score on PC2. Furthermore, the 90% evaporated gasoline standard has greater abundance of the C_3 - and C_4 -alkylbenzenes compared with the other two gasoline standards, as a result of evaporation. Consequently, the 90% evaporated standard is positioned more positively on PC2 than the neat and 10% evaporated gasoline standards.

The kerosene standards are positioned negatively on both PC1 and PC2 in the scores plot due to the negative weighting of the C_{12} – C_{16} normal alkanes in the loadings plots (Fig. 2). The 70% evaporated kerosene standards are positioned slightly more negatively on both PC1 and PC2 due to concentration of the later-eluting alkanes (C_{13} – C_{16}). As these compounds are weighted negatively in the loadings plots, the increased abundance in the standard results in a more negative positioning in the scores plot on both PCs.

The major compounds in lighter fluid that contribute to the positioning on the scores plot are the normal alkanes C_9 – C_{11} .

These three alkanes are weighted positively on PC1 resulting in a positive score for the lighter fluid standards on PC1. On PC2, however, neat and 10% evaporated lighter fluids are positioned negatively in the scores plot, while 90% evaporated lighter fluid is positioned positively. This difference in positioning is explained with reference to the mean-centered data. For all three standards, there is a small negative contribution from 1,3,5-trimethylbenzene, a compound in gasoline that is introduced during the process of mean centering, as well as a positive contribution from C_{10} , a characteristic compound in the lighter fluid. However, in the neat and 10% evaporated standards, the abundance of C_{10} is approximately one order of magnitude less than the abundance in the 90% evaporated standard. When the mean-centered data are multiplied by the eigenvector for PC2, 1,3,5-trimethylbenzene is weighted negatively, while C_{10} is weighted positively. But, for the neat and 10% evaporated standards, the negative contribution from 1,3,5-trimethylbenzene greatly outweighs the small positive contribution from C_{10} . As a result, the neat and 10% evaporated lighter fluid standards have an overall negative score on PC2. In contrast, for the 90% evaporated standard, the positive contribution from C_{10} outweighs the negative contribution from 1,3,5-trimethylbenzene, resulting in an overall positive score for this standard on PC2.

Thus, and as expected, the three liquids can be differentiated by visual examination of the scores plot: lighter fluid is positioned positively on PC1, while gasoline and kerosene are positioned negatively. The latter two liquids are distinguished on PC2 as gasoline is positioned positively and kerosene is positioned negatively. Furthermore, the most evaporated liquid (90% evaporated for gasoline and lighter fluid and 70% evaporated for kerosene) can be distinguished from the neat liquid, due to significant changes in chemical composition as a result of evaporation.

Investigation of Burned Substrate Interference Effects in High-Density Polyethylene

To investigate the burn time that generated a significant number and abundance of interference compounds, samples of HDPE were burned for times ranging from 0 to 120 s (Fig. 3). With no burning, extracts of HDPE are dominated by dodecene, tetradecene, and hexadecene (Fig. 3A). With only 10 s of burning, undecene and pentadecene become more abundant (Fig. 3B), and after 20 s of burning, the characteristic bell-shaped triplet of peaks expected as polyethylene pyrolyzes become apparent (Fig. 3C). During degradation, the polymer undergoes random

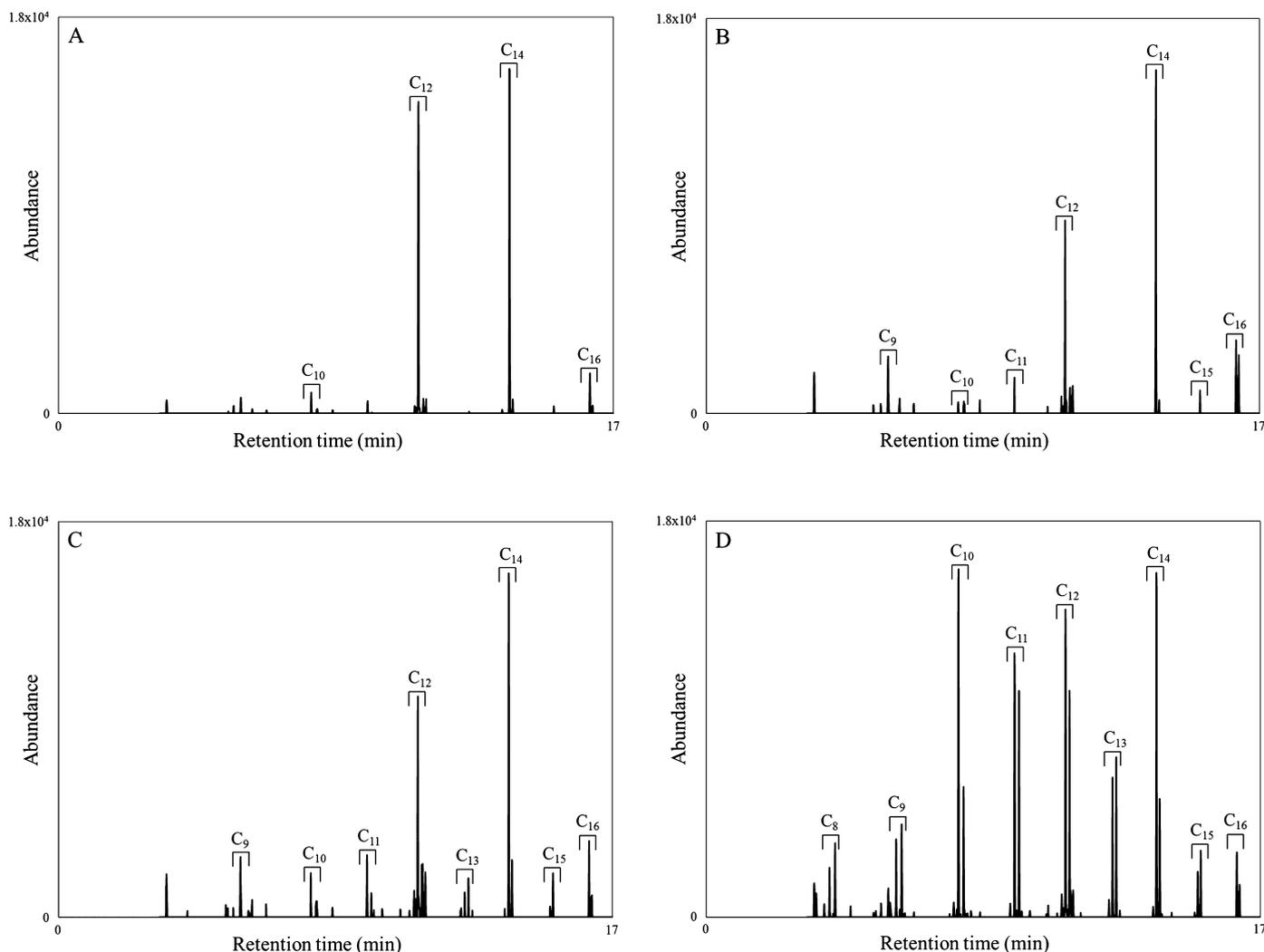


FIG. 3—Total ion chromatograms for high-density polyethylene after burning for (A) 0 s, (B) 10 s, (C) 20 s, and (D) 60 s. Chromatograms are shown in expanded view (0–17 min).

scission, which results in the formation of an alkadiene, an alkene, and an alkane for each carbon number (1). With 30 s of burning, these triplets of peaks become more abundant, and after 60 s of burning, the alkadiene, alkene, and alkane for C₈–C₁₆ are readily visible (Fig. 3D). The abundance of these interference compounds did not significantly increase with further burning up to 120 s, and hence, a burn time of 60 s was deemed appropriate for subsequent studies.

Chromatograms of the simulated ILRs for each liquid are shown in Figure 4. For gasoline and lighter fluid (Fig. 4A and C, respectively), the addition of the later-eluting substrate compounds (alkadienes, alkenes, and alkanes) visually alters the chromatogram compared with the corresponding standards. Furthermore, nonene and decene co-elute with *o*-xylene (a C₂-alkylbenzene in gasoline) and 1,3,5-trimethylbenzene (a C₃-alkylbenzene in gasoline), altering the expected ratios of the C₂- and C₃-alkylbenzenes in this liquid. For kerosene (Fig. 4B), the major difference in the chromatogram of the simulated ILR compared with the standard is the addition of the C₁₀–C₁₆ alkenes. Other compounds in kerosene mask the alkadienes from the substrate. Both the substrate and kerosene contain the normal alkanes C₁₀–C₁₆, and with the additional contribution of these compounds from the substrate, the expected ratio of the alkanes is altered. As a result, identification of kerosene in the simulated fire debris based solely on visual assessment of the total ion chromatogram is difficult.

Association of Simulated ILRs with Corresponding Standard using PCA

The scores plot for the liquid standards with projections for the simulated ILRs is shown in Figure 5. It should be noted that because the plot was generated using the liquid standards alone, only compounds that are present in the standards, and hence in the loadings plot, will affect positioning of the ILRs on the scores plot. That is, interference compounds, which are typically not present in the standards, are essentially eliminated and do not affect positioning of the ILRs on the scores plot.

The simulated ILRs containing gasoline are positioned similarly on PC1 in the scores plot to the corresponding standards. On PC2, however, the neat and 10% evaporated gasoline ILRs are generally more negative than the standards due to the addition of the normal alkane interferences from the HDPE. These alkanes are weighted negatively on both PCs, but have minimal contribution to PC1. Hence, positioning of the neat and 10% evaporated gasoline ILRs in the scores plot is more affected on PC2. Replicates of one extract of the neat gasoline-simulated ILR (labeled 1 in Fig. 5) are positioned more positively on PC2 in the scores plot than the standard and other four neat gasoline ILRs. This particular ILR has greater abundance of toluene and the C₂-alkylbenzenes compared with the other neat gasoline ILRs. As these compounds have low contribution to PC1, positioning of the ILRs is not as affected on PC1. However, on PC2, these compounds have a greater, positive contribution, 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 simulated ILRs containing kerosene are also positioned close to the corresponding standards in the scores plot, albeit slightly more positively on PC2. This is due to the additional presence of toluene, which is present in these extracts as an interference. Toluene is used during production of HDPE, and residues of the solvent are apparent in the TICs of these simu-

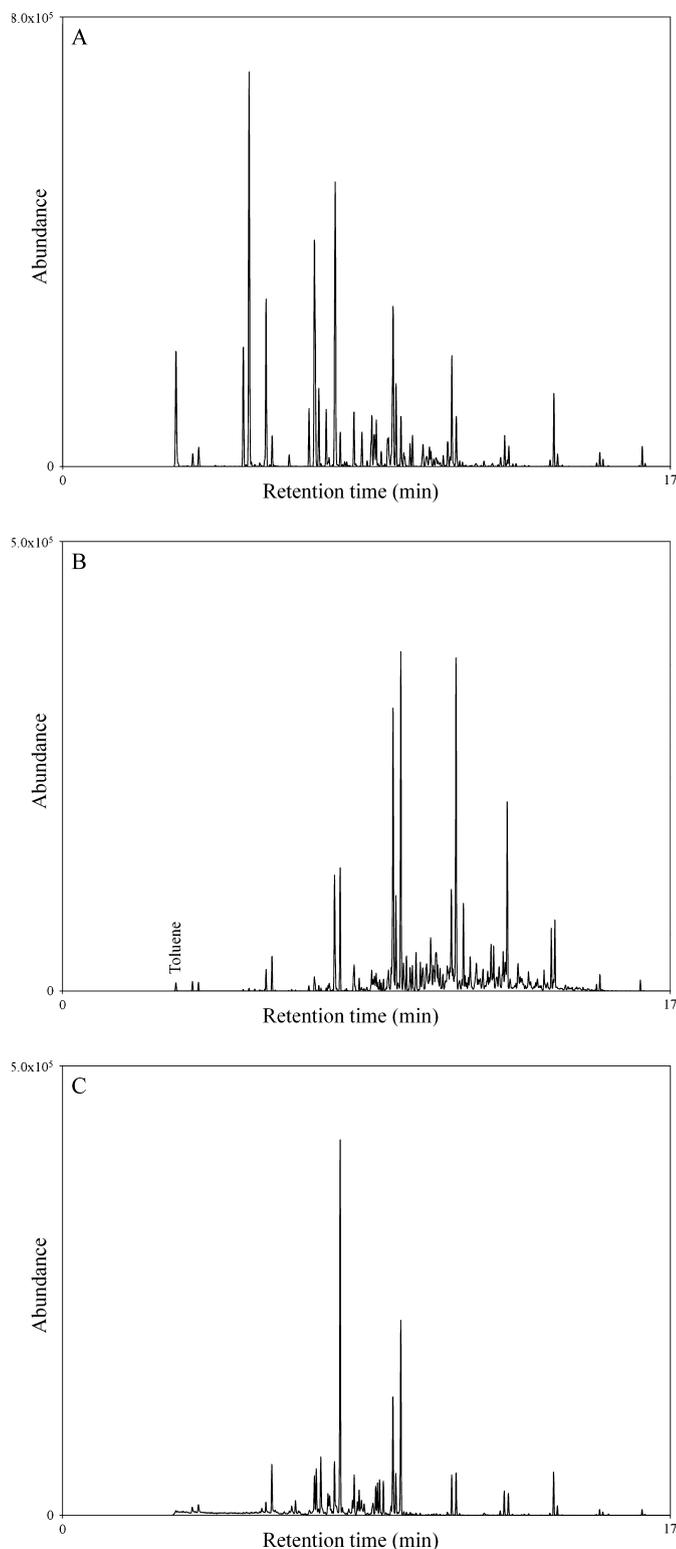


FIG. 4—Representative total ion chromatograms of simulated ignitable liquid residues containing (A) neat gasoline, (B) neat kerosene, and (C) neat lighter fluid. Chromatograms are shown in expanded view (0–17 min).

lated ILRs (Fig. 4B). Toluene is a compound in gasoline and, hence, is present in the loadings plots. As a result, this compound will affect positioning of the kerosene ILRs on the scores plot. Toluene has a positive contribution to PC2 such that the ILRs are positioned more positively than the corresponding standards on PC2 in the scores plot. Despite the slight shift in

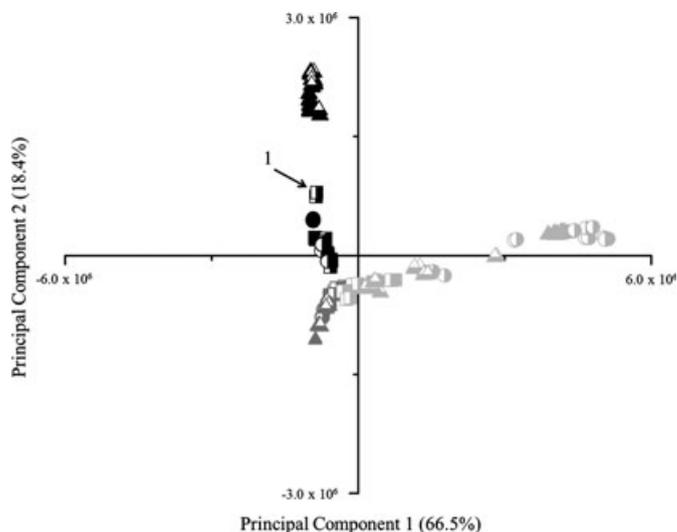


FIG. 5—Scores plot of principal component 1 vs. principal component 2 based on total ion chromatograms for the ignitable liquid standards with scores projected for the simulated ignitable liquid residues ($n = 15$ for each standard and residue). Liquid standards are denoted as filled symbols, while simulated ignitable liquid residues are shown as half-filled symbols. Gasoline is shown in black; kerosene, in dark gray; and lighter fluid, in light gray. Symbols denote the 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.

positioning, it is possible to associate the simulated fire debris samples with the kerosene standards. This begins to demonstrate the potential of statistical procedures to overcome limitations in visual assessment of chromatograms, as discussed previously (Fig. 4).

The neat lighter fluid ILRs are positioned slightly more negatively on PC1 and PC2 in the scores plot than the corresponding standard. 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 a greater abundance of C_{11} than the standard, although the abundance of C_{10} is higher in the standard than in the ILR. Because C_{10} dominates the loadings plot, the lower abundance of this compound in the ILR results in a less positive position in the scores plot. Although the ILR also contains normal alkanes from the substrate, these compounds have low contribution to PC1 and, hence, do not substantially affect positioning of the ILR on this PC in the scores plot.

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

More spread is apparent among replicates of the 10% and 90% evaporated lighter fluid ILRs, particularly in PC1. The former are spread more positively on PC1, and the latter, spread more negatively, than the corresponding standards. This shift in positioning is due to differences in the abundance of the dominant compounds C_9 - C_{11} in the ILRs and the standards. These differences are due to variation introduced as a result of further evaporation of the liquid, as well as thermal degradation and/or pyrolysis of the HDPE matrix.

For 10% evaporated lighter fluid, the abundance of C_9 - C_{11} is greater in the ILRs. Because these compounds are weighted positively on PC1, the higher abundance results in the more positive positioning of the ILRs compared with the standards in the scores plot. The opposite is true for the 90% evaporated lighter fluid as the abundance of C_9 - C_{11} is lower in the ILRs than in the standards, due to further evaporation of the liquid that results in the more negative positioning of the ILRs in the scores plot.

Despite the spread, association of the lighter fluid ILRs with the appropriate liquid is generally possible, although not to the specific evaporation level. However, and based solely on visual assessment of the scores plot, some of the ILRs containing neat and 10% evaporated lighter fluid may be wrongly associated with kerosene. This is primarily due to the presence of normal alkanes in both the lighter fluid ILRs and the kerosene standards, making these liquids appear more chemically similar.

Association of Simulated ILRs with Corresponding Standard using PPMC Coefficients

Mean PPMC coefficients, along with the range in coefficients, were calculated for replicates of each simulated ILR (Table 2). Coefficients are lower than normally expected for replicates ($r = 1.00$), mainly due to variability in the evaporation and thermal degradation and/or pyrolysis processes. Despite this variability, replicates of each simulated ILR show strong correlation ($r > 0.805$). However, the standard deviations associated with the means are relatively large compared with those for the liquid standards (Table 1), which can be attributed to variability in the burning process. When the range of coefficients is also considered, replicates of most ILRs show moderate-to-strong correlation.

Mean PPMC coefficients were also calculated to assess similarity between each simulated ILR and the corresponding standard, as well as similarity to the neat gasoline, neat kerosene, and neat lighter fluid standards (Table 3). Moderate-to-strong correlation is observed between each simulated ILR and the corresponding standard. These lower coefficients are due not only to the presence of substrate interferences in the ILRs, but also to the effects of evaporation and thermal degradation and/or pyrolysis.

The simulated ILRs containing gasoline show moderate correlation to the neat gasoline standard, weak-to-moderate correlation to the neat kerosene standard, and weak correlation to the neat lighter fluid standard. The moderate correlation observed between the simulated ILRs and the neat gasoline standard is

TABLE 2—Mean and range of Pearson product moment correlation coefficients for replicates ($n = 105$) of each liquid extracted from the simulated ignitable liquid residue for the HDPE substrate.

Liquid Extracted from Simulated ILR for HDPE Substrate	Mean PPMC Coefficient \pm Standard Deviation	Range of PPMC Coefficients
Neat gasoline	0.830 \pm 0.165	1.000–0.491
10% evaporated gasoline	0.916 \pm 0.048	1.000–0.830
90% evaporated gasoline	0.966 \pm 0.029	1.000–0.894
Neat kerosene	0.917 \pm 0.064	1.000–0.786
10% evaporated kerosene	0.947 \pm 0.029	1.000–0.906
70% evaporated kerosene	0.872 \pm 0.102	0.999–0.683
Neat lighter fluid	0.816 \pm 0.120	0.995–0.557
10% evaporated lighter fluid	0.841 \pm 0.180	1.000–0.498
90% evaporated lighter fluid	0.805 \pm 0.148	1.000–0.504

TABLE 3—Mean Pearson product moment correlation coefficients for replicates ($n = 225$) of each liquid extracted from the simulated ignitable liquid residue for the HDPE substrate correlated with the corresponding standard, the neat gasoline standard, the neat kerosene standard, and the neat lighter fluid standard.

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

attributed to the presence of the substrate interference compounds. Coefficients are calculated based on a point-by-point comparison of the two chromatograms. As a result, compounds present in one chromatogram, but not in the other, as is the case for the interference compounds, lower the PPMC coefficient. The somewhat higher correlation of the gasoline ILRs with kerosene than with lighter fluid is due to the presence of the normal alkanes as substrate interferences in the simulated ILR, because these alkanes are present in the kerosene standard. Despite moderate correlation to both gasoline and kerosene standards, the actual coefficients are higher for comparison with the neat gasoline standard. Thus, in combination with PCA, it is possible to associate the simulated ILRs containing gasoline more closely with the gasoline standard than with the kerosene standard.

Kerosene-containing simulated ILRs show moderate-to-strong correlation to the corresponding standards. The kerosene ILRs show moderate-to-strong correlation to the neat kerosene standard, but only weak correlation to both the neat gasoline and lighter fluid standards. Therefore, association with the corresponding standard is also possible for these simulated ILRs, mainly because the substrate interferences are compounds that are also characteristic of this liquid and, hence, are present in both the standard and ILR.

The lighter fluid simulated ILRs show moderate correlation to the corresponding standards, which again is expected due to evaporative losses and pyrolysis, as well as the additional presence of the substrate interferences. The lighter fluid ILRs show moderate-to-strong correlation to the neat lighter fluid standard, weak correlation to the neat gasoline standard, and weak-to-moderate correlation to the neat kerosene standard. Thus, it is possible to associate the simulated ILRs containing lighter fluid with the corresponding liquid in the presence of the HDPE substrate using PPMC coefficients.

Discussion

Using PCA, differentiation of the liquid standards was possible according to liquid type (gasoline, kerosene, and lighter fluid), which is reasonable due to distinct differences in chemical composition among the liquids. For all three liquids, the neat and 10% evaporated standards could not be distinguished in the scores plot. However, the most evaporated standard for each liquid (90% for gasoline and lighter fluid and 70% for kerosene) was distinguished from the corresponding neat and 10% evaporated standards due to significant differences in chemical composition as a result of evaporation.

In this study, PCA was performed initially on only the liquid standards, 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 those compounds contributing to the PCs (i.e., present in the loadings plots) will affect positioning of the simulated ILRs on the scores plot. In other words, only compounds present in both the liquid standards and ILRs will affect positioning of the latter. As a result, PCA applied in this way can serve as a filter to minimize or eliminate the effect of substrate interferences.

However, pyrolysis products of the HDPE substrate include normal alkanes, which are also present in kerosene. As a result, the presence of these alkanes affected positioning of the simulated ILRs on the scores plot. The ILRs were generally shifted toward the kerosene standards, although for the gasoline- and kerosene-containing ILRs, association with the corresponding liquid type was still possible by PCA. In contrast, some of the ILRs containing neat and 10% evaporated lighter fluid were positioned closely to the kerosene standards, making association with the appropriate liquid type using PCA alone more difficult.

Pearson product moment correlation coefficients were also used to assess association of the simulated ILRs with the corresponding liquid standard. Because PPMC coefficients assess similarity between pairs of chromatograms, while PCA identifies sources of greatest variation, the two procedures can be considered complementary. However, calculation of the coefficient involves a point-by-point comparison of the two chromatograms under investigation, and hence, the coefficients are adversely affected by the presence of substrate interferences. Nevertheless, each of the simulated ILRs showed stronger correlation with the corresponding neat standard than with the other two neat standards, thus allowing association.

In summary, using the combination of PCA and PPMC coefficients, association of the simulated ILR with the corresponding liquid type, although not with the specific evaporation level, was demonstrated. Furthermore, the challenges associated with this particular substrate were highlighted because the compounds present as substrate interferences were also present in one of the liquid standards under investigation. While these statistical procedures show promise for application in forensic laboratories, a wider variety of substrates, and the associated pyrolysis products, must be investigated in a similar manner. Additionally, the potential of supervised statistical procedures, which build statistical

models that can be used to classify simulated ILRs according to liquid type, should also be investigated.

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