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TECHNICAL NOTE

CRIMINALISTICS

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Effect of Gas Chromatography Temperature Program on the Association and Discrimination of Diesel Samples*†

ABSTRACT: Five diesel samples were analyzed by gas chromatography–mass spectrometry (GC-MS) using six GC temperature programs, aiming to investigate the effect of temperature program on association and discrimination of the samples. Temperature programs varied by ramp rate and incorporated one- or two-step temperature ramps. Pearson product moment correlation coefficients and principal components analysis were used to evaluate differences in discrimination among the diesel samples afforded by each temperature program, based on the total ion chromatogram (TIC) and selected extracted ion profiles (EIPs). Association of diesel replicates and discrimination among samples based on the TIC and aromatic EIP were similar for all temperature programs based on scores plots. The alkane EIP was not useful in discriminating samples regardless of temperature program, because of similar alkane content of the diesel samples. The association and discrimination of diesel samples was largely unaffected by temperature programs that incorporated one- or two-step temperature ramps.

KEYWORDS: forensic science, fire debris analysis, diesel, gas chromatography–mass spectrometry, Pearson product moment correlation, principal components analysis

Ignitable liquid residues (ILRs) extracted from fire debris are routinely analyzed by gas chromatography–mass spectrometry (GC-MS). The resulting total ion chromatograms (TICs) and extracted ion profiles (EIPs) of characteristic compound classes are visually examined and compared with a reference collection to identify the class of ignitable liquid present. However, such visual assessment is notoriously difficult and often subjective, for a number of reasons. Volatile components of the ignitable liquid are lost during the burning process, changing the chromatogram of the ignitable liquid compared with its neat counterpart. Burned matrices such as carpet or clothing often present chromatograms similar to that of an ignitable liquid because of peaks from inherent hydrocarbons, pyrolysis products, or thermal degradation products (1). The overall aim of this research is to develop an objective method to associate ILRs to neat ignitable liquids while differentiating from such matrix interferences. Statistical and chemometric procedures, including Pearson product moment correlation (PPMC) coefficients and principal components analysis (PCA) will be applied to the chromatographic data to remove the subjectivity associated with visual comparisons. The first stage of this research has focused on determining an appropriate GC temperature program that allows the association and discrimination of one type of ignitable liquid from different sources. Future studies will apply the aforementioned statistical and chemometric procedures to investigate the association and discrimination of ignitable liquids even in the presence of matrix interferences.

Several GC temperature programs exist for analyzing ignitable liquids which range from 30 min to 2 h (2,3). A longer temperature program is not ideal since fast analysis times are preferred to prevent or minimize case backlogs. However, with a shorter temperature program, chromatographic resolution is lost, which may decrease inherent variation that is observed among ignitable liquids, especially those that are similar in chemical composition. The loss of such discriminatory information may lead to a misclassification or even misidentification of an ignitable liquid in the sample.

The research reported herein focuses on minimizing the analysis time while still retaining sufficient chemical information for the association and discrimination of ignitable liquids. Five diesel samples were analyzed in triplicate using six different GC temperature programs. Temperature programs varied in the ramp rate as well as the number of ramp steps (one- and two-step ramps). One type of ignitable liquid was chosen for this initial study because successful association and discrimination of samples with very similar chemical composition indicates that this procedure will be successful with ignitable liquids from different classes. Diesel was chosen as the ignitable liquid to analyze because of its complex chemical composition and wide range of boiling points. The TIC and EIPs of characteristic alkane and aromatic compound classes were generated for all samples. EIPs were studied to determine the class of compounds that varied most among diesel samples and, therefore, would be useful for discrimination.

Prior to statistical and chemometric procedures, the TIC and EIP were subjected to three data pretreatment steps: retention time alignment, normalization, and mean-centering (4). Retention time alignment corrects drifts in retention time from run to run and normalization accounts for variation in injection volume. The data were mean-centered prior to PCA to center the variance around

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zero rather than the mean. This ensures that PCA explains the maximum variation from the origin rather than describing the mean.

PPMC coefficients were calculated for the aligned data to assess similarity among samples. This pair-wise comparison of chromatograms may be directly applicable in crime labs for the comparison of a known ignitable liquid to a questioned ILR. PCA was applied to the TIC and EIPs to determine the extent of association and discrimination among the diesel samples afforded by each temperature program. PCA was applied to the complete data set to assess the variation among the diesel samples, which is more useful for determining the class of an unknown ILR by comparing it to a reference collection.

Materials and Methods

Sample Collection

Diesel samples were collected from four different brands of service station in the Lansing, Michigan area. For one brand, samples were collected at two locations, giving a total of five diesel samples. Approximately one-half gallon of each sample was collected and stored in an acid-washed amber bottle at 4°C until analysis. Samples were diluted 10:1 in dichloromethane (spectrophotometric grade, Sigma-Aldrich, St. Louis, MO) prior to GC-MS analysis.

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), 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 diesel sample was manually injected in splitless mode. Six different GC temperature programs were investigated. Each temperature program had an initial temperature of 40°C and a final temperature of 280°C, with the ramp rate varying in each program. The programs were developed based on a two-step temperature program available in the literature (4) and a one-step temperature program used by the National Center for Forensic Sciences (NCFS) for their Ignitable Liquids Reference Collection (2). The ramp rates of the two-step program were increased from 2 and 3°C/min (Method A) to 5 and 10°C/min (Method B). A single-step temperature ramp consistent with the NCFS temperature program parameters except with a slower ramp rate of 5°C/min (Method C) was investigated. The temperature ramp rate of the NCFS program was increased from 10°C/min (Method D) to 20°C/min (Method E) and to 30°C/min (Method F). Faster ramp rates were not investigated as the limit of the GC oven was 30°C/min. Each of the five diesel samples was analyzed in triplicate using each of the six GC temperature programs which are summarized in Table 1.

TABLE 1—*GC temperature programs investigated.*

Method	Initial Temp. (°C)	Initial Hold (min)	Ramp Rate (°C/min)	Final Temp. (°C)	Final Hold (min)	Total Time (min)
A	40	0	2 (to 150°C), 3	280	15	113
B	40	0	5 (to 150°C), 10	280	15	50
C	40	3	5	280	4	55
D	40	3	10	280	4	31
E	40	3	20	280	4	19
F	40	3	30	280	4	15

The transfer line between the GC column and the mass spectrometer was maintained at a temperature of 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. Diesel samples were reanalyzed by Methods E and F, increasing the scan rate to 5.51 scans/sec. This was deemed necessary as initial analysis indicated that more data points were necessary to define each peak for acceptable alignment.

Data Analysis

For each diesel sample analyzed by each GC temperature program, alkane EIP (m/z 57 + 71 + 85 + 99) and aromatic EIP (m/z 91 + 105 + 119 + 133) were generated in ChemStation software (Agilent Technologies). The TIC and EIPs for diesel samples were compiled into individual data sets in Microsoft Excel (Microsoft Corp., Redmond, WA), resulting in three files for each of the six GC temperature programs. The chromatograms of the diesel samples were retention time aligned using an algorithm available in the literature (5). Matlab (version 7.4.0.287; MathWorks, Natick, MA) was used to align the chromatograms as well as to calculate PPMC coefficients as described by Hupp et al. (4). A full table of PPMC coefficients from this research is available in Appendices 1–3. After alignment, each set of chromatograms was peak area normalized and mean-centered. PCA was performed on the mean-centered data using Matlab. PCA scores and loadings plots were generated for the TIC and alkane and aromatic EIPs in Microsoft Excel for each GC temperature program.

Results and Discussion

Figure 1 shows the TIC of one diesel sample analyzed by Methods A, D, and F. These chromatograms represent slow two-step (2, 3°C/min), medium single-step (10°C/min), and fast single-step (30°C/min) temperature ramps. Figure 2 shows the alkane and aromatic EIP for Method D to highlight the alkane and aromatic content in the chromatogram. The normal alkanes (C_9-C_{24}) are visible in a distribution that is characteristic of a diesel chromatogram (Fig. 2*a*). However, a loss of resolution is apparent as ramp rate increases, which is evident from the rising baseline in Fig. 1*b,c*. The aromatic content of the diesel is observed at the beginning of the chromatogram (Fig. 2*b*). The aromatic content is observed with better resolution in Fig. 1*a* because of the slower ramp rate in Method A, which could affect association and discrimination of diesel samples.

Association and Discrimination of Diesel Samples Based on Total Ion Chromatogram

Figure 3*a* shows a section of the TIC for a set of five well-aligned diesel samples analyzed by Method D. As the ramp rate increased to 30°C/min, chromatograms did not align as well (Fig. 3*b*), indicating that the increased ramp rate and resulting loss of resolution negatively affected the alignment. The poor alignment was reflected in subsequent PPMC and PCA results, which will be discussed later.

The PPMC coefficients calculated between pairs of chromatograms were consistently higher between replicates of one diesel than among different diesel samples, as expected, regardless of ramp rate or number of ramp steps. PPMC coefficients tended to increase for faster GC temperature programs. For example, the average PPMC coefficient between Diesels 2 and 4 for Method D

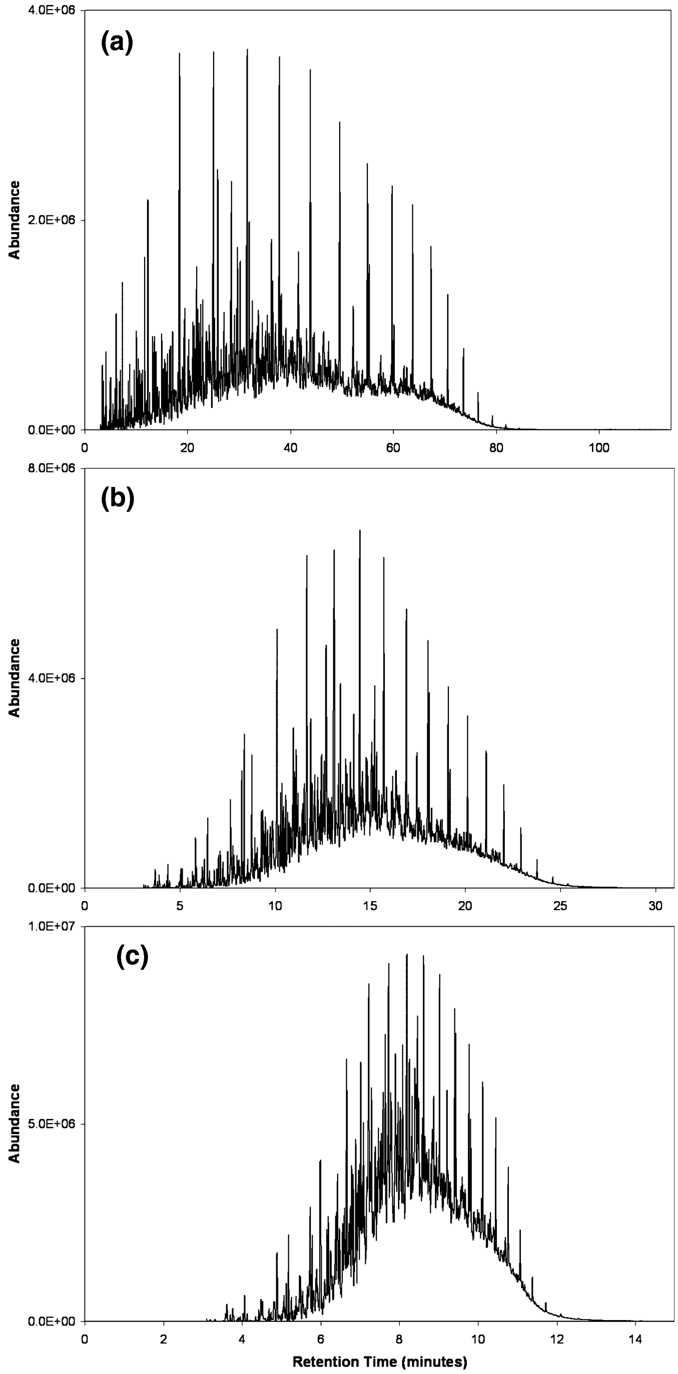

FIG. 1—*Total ion chromatogram of one diesel sample analyzed by (a) method A, (b) method D, and (c) method (F).*

was 0.9126 ± 0.0020. The average PPMC coefficient increased to 0.9309 ± 0.0021 for Method E, and finally to 0.9489 ± 0.0053 for Method F. With faster ramp rates, the diesels appeared more similar because of the corresponding loss of chromatographic resolution. Overall, PPMC coefficients were affected by the loss of resolution resulting from faster ramp rates rather than the number of ramp steps.

The clustering of diesel samples in the PCA scores plots based on the TIC was similar for all GC temperature programs. Replicates of each diesel were clustered closely while different diesels were well separated. No difference in association and discrimination of diesel samples was observed for one- or two-step temperature ramps. Exemplar scores plots for Methods A, D, and F are shown in Fig. 4. Slight spread in the second principal component was observed for the replicates which may be in part because of the manual injection technique. However, there was no overlap among different diesel samples, allowing for discrimination of the five samples, even with the fastest ramp rate. The scores plots for Methods E and F showed greater spread among replicate samples. Visual assessment of the aligned chromatograms for these two temperature programs indicated peak misalignments (Fig. 3*b*), which may have contributed to the spread among replicate samples. Hence, poor alignment may limit the utility of PCA in differentiating diesel samples for faster temperature ramp rates.

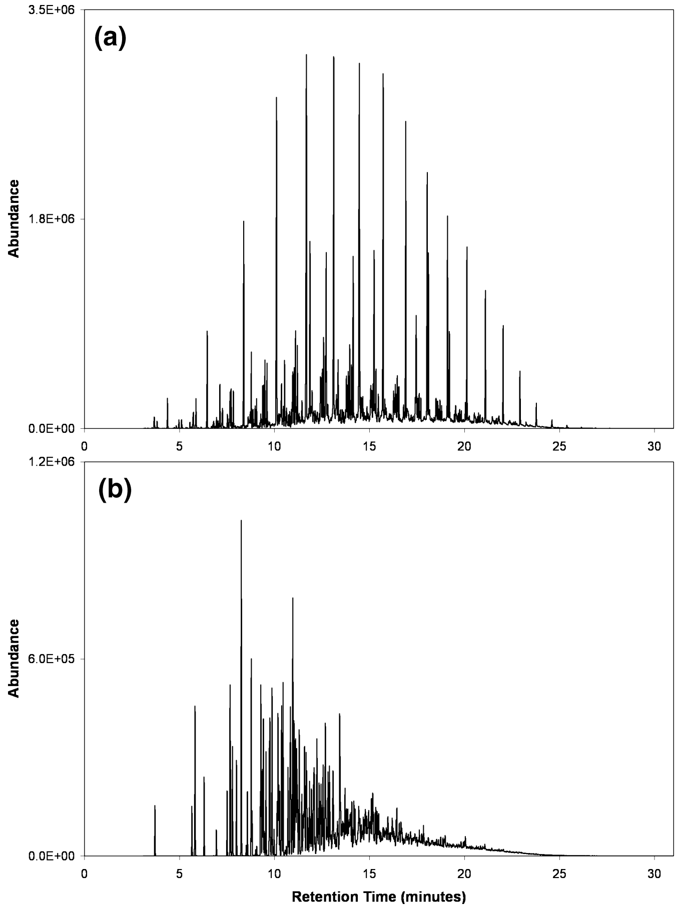

FIG. 2—*(a) Alkane extracted ion profiles (EIP) and (b) aromatic EIP of one diesel sample analyzed by Method D.*

The PPMC coefficients were consistent with the association and discrimination of diesel samples in the PCA scores plots. For Method D, the highest PPMC coefficients were between Diesels 3 and 5 (0.9893 ± 0.0020), which corresponded to the diesel samples that were clustered closest together in the scores plot. The lowest PPMC coefficients were between Diesels 2 and 4 (0.9126 ± 0.0026), which corresponded to the samples that were furthest apart.

The PCA loadings plots for the first principal component for each GC temperature program were generated to identify chemical components contributing most to the variance among samples. For all temperature programs, the loadings plots were dominated by the C_{11}-C_{13} normal alkanes with some contributions from aromatic compounds such as trimethylbenzene and other alkylbenzenes (Fig. 5). The loadings plots for Methods E and F showed a high

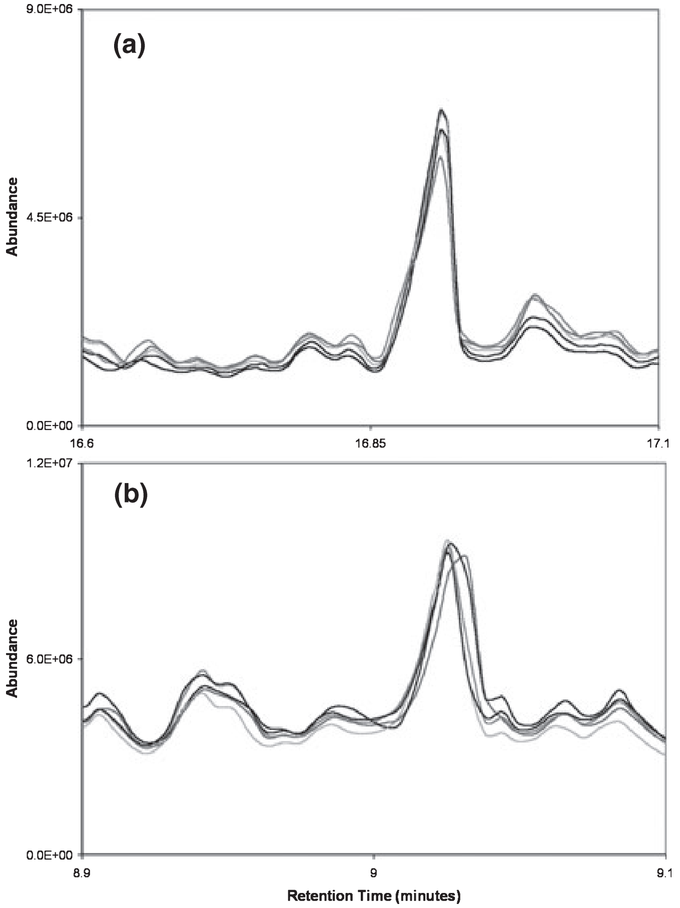

FIG. 3—*(a) Well-aligned hexadecane peak in the total ion chromatogram (TIC) for five diesel samples analyzed by Method D, and (b) poorly aligned hexadecane peak in the TIC of five diesel samples analyzed by Method F.*

occurrence of derivative-shaped curves (Fig. 6). Visual assessment of the corresponding retention time aligned chromatograms confirmed that derivative-shaped curves in the loadings plots were indicative of peak misalignments (Fig. 3).

Alkane Extracted Ion Profile

Several of the trends observed in the TIC were also observed for the alkane EIP. Peak alignment was increasingly worse as the GC temperature ramp rate increased. PPMC coefficients between replicates of the same diesel were generally lower for the alkane EIP than the TIC for all temperature programs, which would indicate less similarity among replicates. Visual examination of the retention time-aligned alkane EIP showed greater misalignments than for the TIC, which may have resulted in lower PPMC coefficients. Nevertheless, PPMC coefficients for the alkane EIP were higher between replicates of the same diesel and lower between different diesels, as expected.

The PCA based on the alkane EIP did not offer discrimination among four of the diesel samples as shown in the scores plot for Method D (Fig. 7). This lack of discrimination was observed in all temperature programs, regardless of ramp rate or the number of ramp steps. As the alkane content is so similar among diesels, PCA is forced to find differences among replicates, causing greater spread in the scores plots. Although manual injection may have contributed to some of the spread in the scores plot, it is clearly not the sole cause of the spread observed for the alkane EIP when compared with the TIC (Fig. 4*b*).

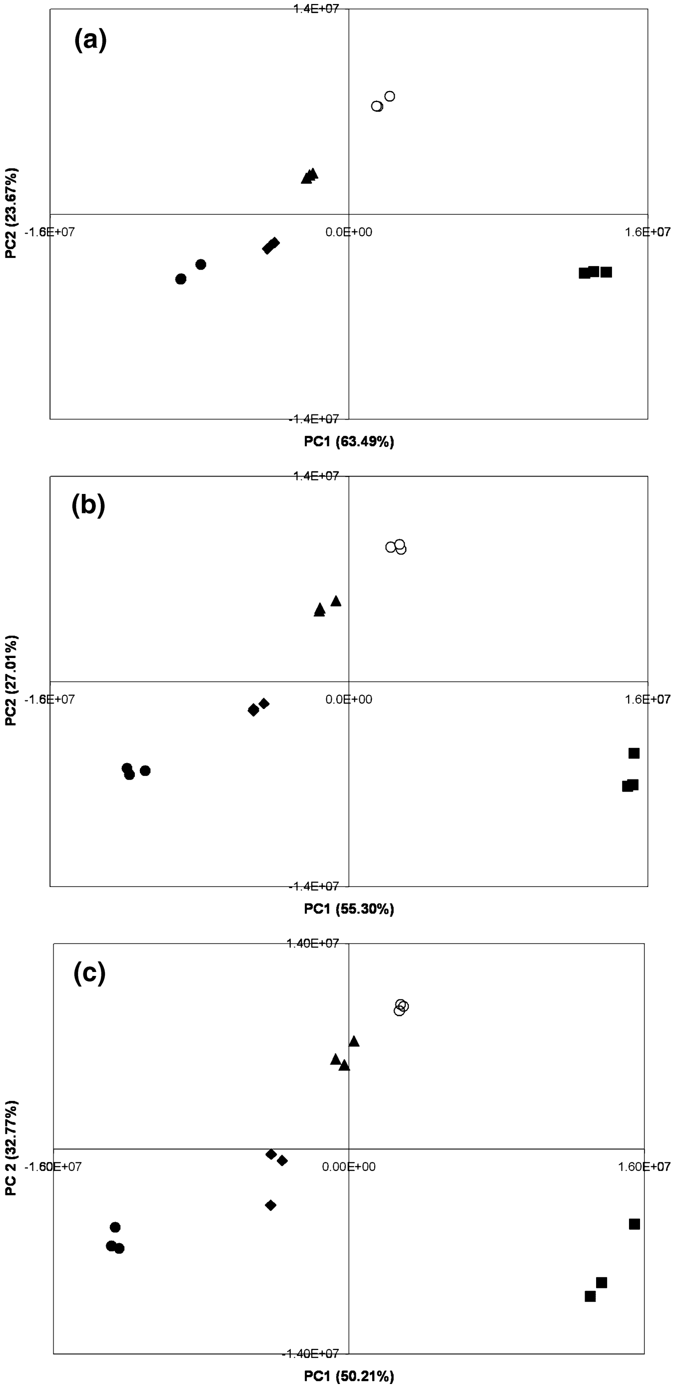

FIG. 4—*Principal components analysis scores plot based on total ion chromatogram for five diesel samples analyzed by (a) Method A, (b) Method D, and (c) Method F. Diesel 1 (♦), Diesel 2 (■), Diesel 3 (▲), Diesel 4 (•), Diesel 5 (○).*

Again, the association and discrimination of the diesel samples in the scores plot was similar for all temperature programs and some overlap was observed among different diesel samples. In the scores plot, one replicate of Diesel 5 (indicated by asterisk in Fig. 7) was closer to a replicate of Diesel 3 than to the other replicates of the same diesel sample. The PPMC coefficient between these two samples was 0.9933. This was higher than the average

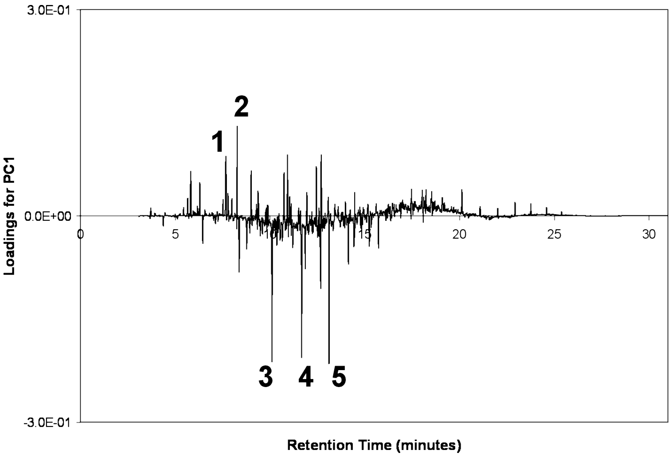

FIG. 5—*Loadings plot of the first principal component for five diesel samples analyzed by Method D, identifying the components contributing the most to the variance in the sample set: (1) 1-ethyl, 3-methylbenzene, (2) 1,3,5-trimethylbenzene, (3) undecane, (4) dodecane, and (5) tridecane.*

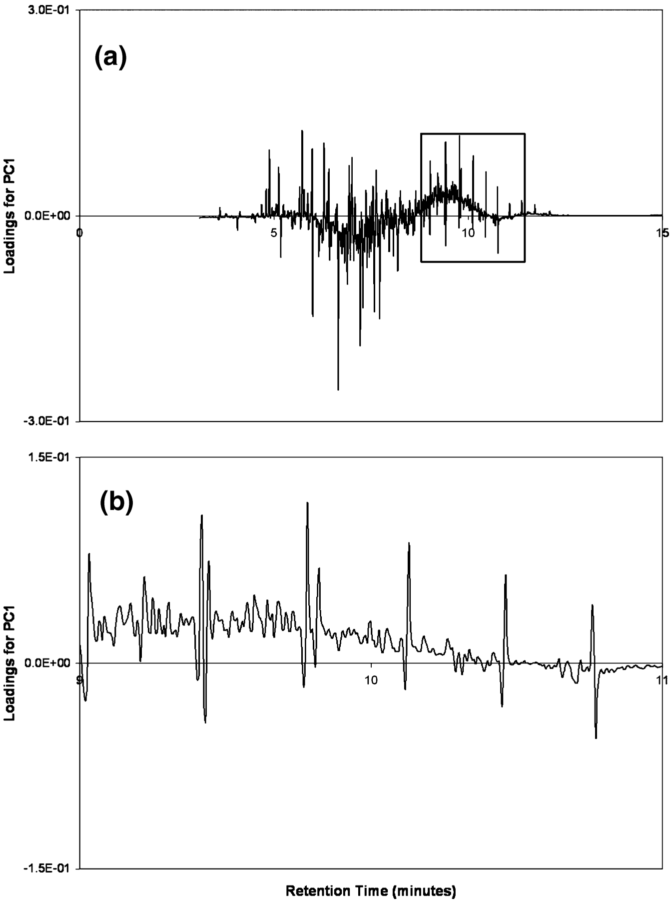

FIG. 6—*(a) Loadings plot of the first principal component for five diesel samples analyzed by Method F, (b) a magnified section of the loadings plot from (a), demonstrating derivative-shaped curves indicative of peak misalignments.*

PPMC coefficient for the replicates of each diesel sample (0.9901 ± 0.0053 for replicates of Diesel 3 and 0.9871 ± 0.0086 for Diesel 5) and reinforces the similarity of alkane content among diesel samples.

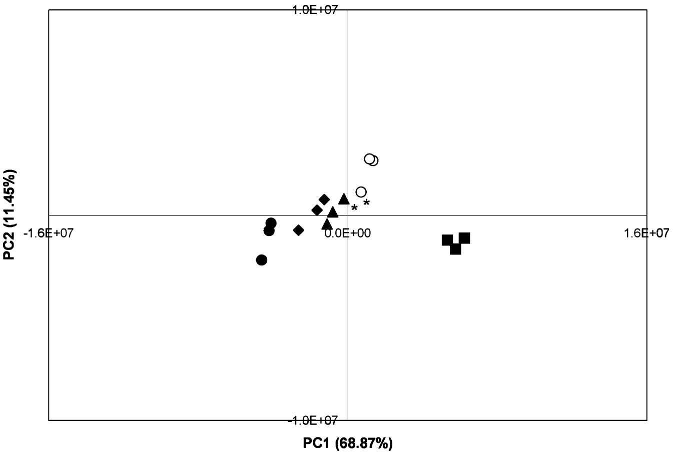

FIG. 7—*Principal components analysis scores plot based on the alkane extracted ion profile for five diesel samples analyzed by Method D. Diesel 1 (◆), Diesel 2 (■), Diesel 3 (▲), Diesel 4 (●), Diesel 5 (○).*

As with the TIC, PPMC coefficients for the alkane EIP were consistent with association and discrimination of the diesel samples in the scores plot. For Method D, Diesels 2 and 4 had the lowest PPMC coefficients (0.8555 ± 0.0154) and were furthest apart in the scores plot, whereas Diesels 1 and 3 had the highest PPMC coefficients (0.9864 ± 0.0042) and were closest. The two diesels with the highest average PPMC coefficient varied by temperature program. For Methods A, B, C, and D, Diesels 1 and 3 had the highest average PPMC coefficient. For Methods E and F, Diesels 3 and 5 had the highest average PPMC coefficient. The pair of diesels with the highest average PPMC coefficient changed with the fastest temperature programs, which may have been a result of the loss of resolution observed for Methods E and F.

In the loadings plot for the first principal component, more volatile hydrocarbons contributed most to the variance among the diesel samples. This was consistent for all temperature programs. Normal alkanes C_{11}-C_{15} dominated the variance, while the less volatile alkanes (C_{16}-C_{24}) contributed less to the variance. Like the TIC, loadings plots for the alkane EIP showed derivative-shaped curves indicative of peak misalignments.

Overall, the alkane profile did not provide any further information in distinguishing the diesel samples than the TIC for any of the temperature programs. The similar alkane content among diesel samples caused spread in the replicates in the scores plot, making association and discrimination of the diesel samples difficult.

Aromatic Extracted Ion Profile

Many of the same trends observed for the TIC and alkane EIP were also observed for the aromatic EIP. PPMC coefficients between replicates of a diesel were consistently higher than the coefficients between different diesels. PPMC coefficients between replicates of the same diesel for the aromatic EIP were higher than the alkane EIP, though lower than the TIC. However, PPMC coefficients between different diesel samples were lowest for the aromatic EIP and also had a greater range of PPMC coefficients than the alkane EIP or TIC. A greater range of PPMC coefficients indicated a greater variation in aromatic content among the diesel samples and suggested that the aromatic EIP could be more useful than the alkane EIP for discriminating diesel samples.

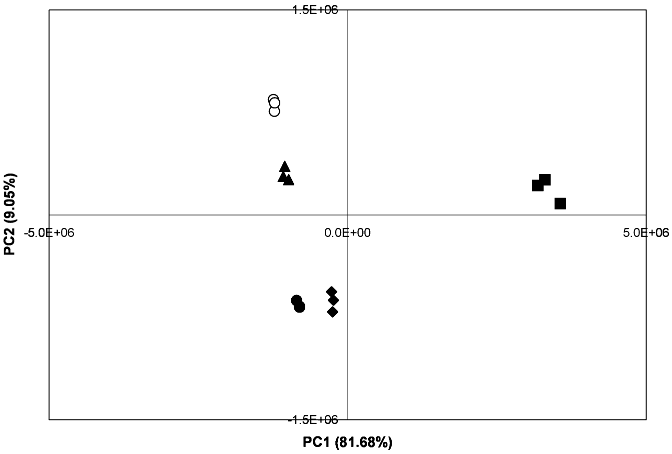

FIG. 8—*Principal components analysis scores plot based on the aromatic extracted ion profiles for five diesel samples analyzed by Method D. Diesel 1 (◆), Diesel 2 (■), Diesel 3 (▲), Diesel 4 (●), Diesel 5 (○).*

Scores plots for the aromatic EIP showed the same general pattern for all GC temperature programs. The scores plot of the aromatic EIP for Method D is shown in Fig. 8. Again, replicates of each diesel were associated while different diesels were discriminated in the scores plots. This association and discrimination was similar for all temperature programs, irrespective of ramp rate or the number of ramp steps.

The PPMC coefficients were consistent with clustering in the PCA scores plot. The highest PPMC coefficients corresponded to the diesels that were clustered closest together on the first principal component. For Method D, Diesels 3 and 5 had the highest PPMC coefficients (0.9894 ± 0.0026) and were positioned closest in the scores plot. Diesels 2 and 5 had the lowest PPMC coefficients for Method D (0.8481 ± 0.0051) and were furthest apart. For comparison, Diesels 2 and 4 had the lowest average PPMC coefficients for the TIC and alkane EIP. As different information was obtained from the aromatic EIP than from the TIC and alkane EIP, the use of different EIPs is valuable in the association and discrimination of diesel samples.

The loadings plots for the first principal component for the aromatic EIP also showed the same general pattern for all GC temperature programs. The compounds that contributed the most to the variance were xylene, trimethylbenzene, and other alkylbenzenes. Again, derivative-shaped curves were prevalent in the loadings plots for the fastest temperature programs (Methods E and F), indicating peak misalignments, which was confirmed by visual assessment of the aligned EIP.

From the PPMC and PCA results, the aromatic content among diesels was more variable than the alkane content. As a result, the aromatic EIP offered additional discriminatory information to supplement the information gained from the TIC in differentiating diesel samples.

Increased Mass Spectrometry Scan Rate

Peak misalignments were prevalent in the TIC and EIPs for the fastest temperature programs. Upon closer inspection of the aligned chromatograms of Methods E and F, it was observed that there were insufficient data points defining a peak to align the chromatograms satisfactorily. Therefore, the scan rate of the mass spectrometer was increased from 2.91 to 5.51 scans/sec resulting in a change from approximately six points across a peak for the slower scan rate to approximately 12 points across a peak for the faster scan rate (6). In Fig. 9*a*, a poorly aligned section of the TIC for

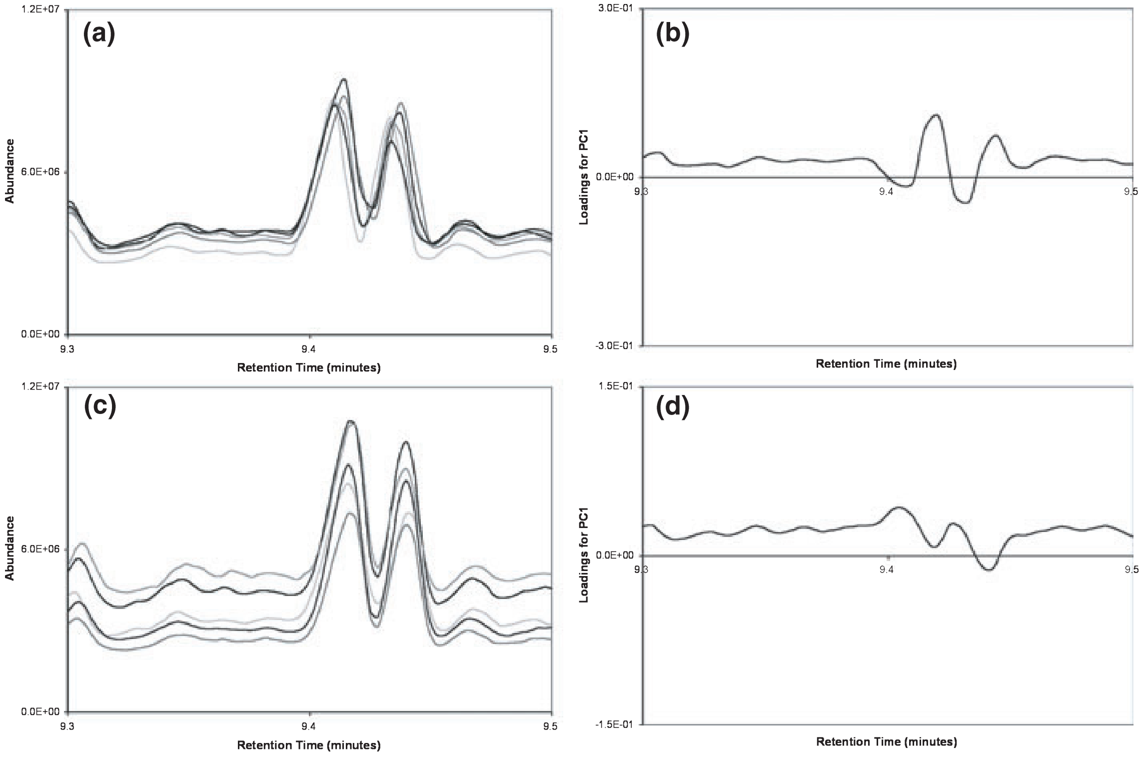

FIG. 9—*(a) Section of aligned total ion chromatogram (TIC) of five diesel samples analyzed by Method F with a scan rate of 2.91 scans/sec showing poor alignment. (b) Loadings plot showing the derivative-shaped curve indicative of the peak misalignment in (a). (c) Same section of the TIC, showing the aligned chromatograms of five diesel samples analyzed by Method F with a scan rate of 5.51 scans/sec. (d) Loadings plot without any derivative-shaped curves indicating an improvement in alignment.*

Method F is shown with the corresponding derivative-shaped curve in the loadings plot (Fig. 9*b*). Using the faster scan rate, the alignment of these peaks is improved (Fig. 9*c*), which is reflected in the loadings plot by the improvement of the derivative-shaped curve (Fig. 9*d*). Overall, there was little change in the loadings plots with a faster scan rate, though fewer derivative-shaped curves were apparent, indicating some improvement in the alignment. This was further verified by visual comparison of the aligned chromatograms. However, similar association and discrimination of diesel samples was observed in the scores plots for the TIC, alkane, and aromatic EIPs as described previously. Spread was still observed in the replicates for the TIC, alkane, and aromatic EIP indicating that an increase in the scan rate did not correct all misalignments. The manual injection technique may explain other misalignments not corrected by the increased scan rate.

Conclusions

The association and discrimination of five diesel samples was not greatly affected by GC temperature ramp rate or number of ramp steps. The average PPMC coefficients between replicates of the same diesel were generally higher than those between different diesel samples and PPMC results were consistent with the results of PCA. The PCA scores plots showed similar association and discrimination of the five diesel samples and PCA loadings plots identified the same components (C_{11}-C_{15} normal alkanes and alkylbenzenes) as contributing to the variance among diesel samples for each GC temperature program. Both the TIC and aromatic EIP offered valuable discriminatory information, whereas the alkane profile was not useful in distinguishing diesels because of the similar alkane content among diesels. The fastest GC ramp rates (Method E and Method F) showed an obvious loss of resolution. However, the clustering of the diesel samples in the scores plot and components contributing the most to the variance in the loadings plots were comparable to the slowest GC ramp rate (Method A). Although the slowest GC ramp rates offered improved resolution, the total analysis time (113 min) is not feasible for fire debris analyses. For Methods E and F (the fastest ramp rates), it was necessary to increase the scan rate of the mass spectrometer to sufficiently improve alignment of chromatograms. Therefore, Method D was determined to be the most appropriate program for fire debris analysis. This method offered adequate association and discrimination without any change in mass spectrometer instrument parameters from the method currently used by the NCFS.

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Appendix 1

PPMC coefficients for TIC of five diesel samples analyzed by Methods A, D, and F. Plain font indicates Method A, bold font indicates Method D, and italicized font indicates Method F.

Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	
0.9976 ± 0.0003	0.9120 ± 0.0048	0.9887 ± 0.0007	0.9806 ± 0.0013	0.9585 ± 0.0043	Diesel 1
0.9943 ± 0.0010	**0.9425 ± 0.0012**	**0.9851 ± 0.0041**	**0.9808 ± 0.0027**	**0.9708 ± 0.0009**	
0.9961 ± 0.0024	*0.9689 ± 0.0035*	*0.9912 ± 0.0027*	0.9870 ± 0.0026	0.9822 ± 0.0030	
	0.9930 ± 0.0023	0.9193 ± 0.0047	0.8691 ± 0.0063	0.9259 ± 0.0024	Diesel 2
	0.9943 ± 0.0017	**0.9463 ± 0.0026**	**0.9126 ± 0.0026**	**0.9482 ± 0.0033**	
	0.9897 ± 0.0064	*0.9687 ± 0.0011*	0.9489 ± 0.0053	0.9674 ± 0.0011	
		0.9980 ± 0.0007	0.9676 ± 0.0017	0.9802 ± 0.0042	Diesel 3
		0.9930 ± 0.0016	**0.9661 ± 0.0021**	**0.9893 ± 0.0020**	
		0.9985 ± 0.0008	0.9760 ± 0.0022	0.9965 ± 0.0012	
			0.9956 ± 0.0025	0.9299 ± 0.0064	Diesel 4
			0.9952 ± 0.0023	**0.9455 ± 0.0018**	
			0.9988 ± 0.0008	0.9652 ± 0.0012	
				0.9950 ± 0.0012	Diesel 5
				0.9965 ± 0.0005	
				0.9995 ± 0.0003	

Appendix 2

PPMC coefficients for alkane EIP of five diesel samples analyzed by Methods A, D, and F. Plain font indicates Method A, bold font indicates Method D, and italicized font indicates Method F.

Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	
0.9927 ± 0.0031 **0.9850 ± 0.0021** *0.9753 ± 0.0121*	0.8875 ± 0.0081 **0.9103 ± 0.0042** *0.9007 ± 0.0205*	0.9934 ± 0.0017 **0.9864 ± 0.0042** *0.9792 ± 0.0090*	0.9782 ± 0.0035 **0.9758 ± 0.0091** *0.9681 ± 0.0144*	0.9376 ± 0.0259 **0.9705 ± 0.0083** *0.9584 ± 0.0109*	Diesel 1
	0.9841 ± 0.0088 **0.9913 ± 0.0008** *0.9835 ± 0.0096*	0.9015 ± 0.0076 **0.9259 ± 0.0120** *0.8995 ± 0.0077*	0.8360 ± 0.0114 **0.8555 ± 0.0154** *0.8499 ± 0.0242*	0.9227 ± 0.0169 **0.9368 ± 0.0070** *0.9160 ± 0.0014*	Diesel 2
		0.9964 ± 0.0013 **0.9901 ± 0.0053** *0.9896 ± 0.0067*	0.9754 ± 0.0038 **0.9687 ± 0.0083** *0.9699 ± 0.0056*	0.9430 ± 0.0264 **0.9782 ± 0.0087** *0.9792 ± 0.0128*	Diesel 3
			0.9913 ± 0.0036 **0.9921 ± 0.0063** *0.9800 ± 0.0104*	0.9243 ± 0.0180 **0.9414 ± 0.0140** *0.9490 ± 0.0112*	Diesel 4
				0.9688 ± 0.0199 **0.9871 ± 0.0085** *0.9946 ± 0.0034*	Diesel 5

Appendix 3

PPMC coefficients for aromatic EIP of five diesel samples analyzed by Methods A, D, and F. Plain font indicates Method A, bold font indicates Method D, and italicized font indicates Method F.

Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	
0.9957 ± 0.0013 **0.9947 ± 0.0023** *0.9954 ± 0.0027*	0.9161 ± 0.0020 **0.9032 ± 0.0041** *0.9086 ± 0.0040*	0.9772 ± 0.0011 **0.9763 ± 0.0039** *0.9787 ± 0.0040*	0.9825 ± 0.0012 **0.9824 ± 0.0017** *0.9880 ± 0.0023*	0.9551 ± 0.0014 **0.9593 ± 0.0020** *0.9600 ± 0.0048*	Diesel 1
	0.9963 ± 0.0013 **0.9891 ± 0.0022** *0.9828 ± 0.0085*	0.8725 ± 0.0033 **0.8634 ± 0.0057** *0.8633 ± 0.0056*	0.8611 ± 0.0032 **0.8626 ± 0.0046** *0.8685 ± 0.0027*	0.8487 ± 0.0026 **0.8481 ± 0.0051** *0.8441 ± 0.0043*	Diesel 2
		0.9957 ± 0.0009 **0.9924 ± 0.0034** *0.9959 ± 0.0030*	0.9830 ± 0.0010 **0.9829 ± 0.0019** *0.9837 ± 0.0045*	0.9904 ± 0.0018 **0.9894 ± 0.0026** *0.9935 ± 0.0029*	Diesel 3
			0.9957 ± 0.0008 **0.9931 ± 0.0049** *0.9979 ± 0.0013*	0.9671 ± 0.0030 **0.9691 ± 0.0011** *0.9686 ± 0.0047*	Diesel 4
				0.9924 ± 0.0028 **0.9945 ± 0.0016** *0.9987 ± 0.0006*	Diesel 5