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ASSOCIATION AND DISCRIMINATION OF DIESEL FUELS USING CHEMOMETRIC PROCEDURES FOR FORENSIC ARSON INVESTIGATIONS

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ASSOCIATION AND DISCRIMINATION OF DIESEL FUELS USING CHEMOMETRIC PROCEDURES FOR FORENSIC ARSON INVESTIGATIONS

By

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ABSTRACT

ASSOCIATION AND DISCRIMINATION OF DIESEL FUELS USING CHEMOMETRIC PROCEDURES FOR FORENSIC ARSON INVESTIGATIONS

By

Lucas James Marshall

The identification of an ignitable liquid in fire debris is indicative of an intentional fire and hence, is significant evidence in arson investigations. Currently, gas chromatography-mass spectrometry (GC-MS) is the conventional analytical technique used for the identification of ignitable liquids through chromatographic pattern matching. Chemometric procedures such as Pearson Product Moment Correlation (PPMC) coefficients and Principal Components Analysis (PCA) provide a more objective method to statistically associate and discriminate burned and unburned diesel fuels based on chemical composition in both the total ion chromatogram (TIC), as well as extracted ion profiles (EIP) corresponding to characteristic compound classes in the diesel samples. Data pre-treatment options, such as retention time alignment and area normalization, were also investigated in order to determine their effects on the chemometric results.

The association and discrimination of burned and unburned diesels was also examined. Diesels were spiked onto different matrices commonly found in the home (cotton cloth, magazine, and carpet) and burned in order to simulate arson conditions. The burned diesels were extracted using solvent extraction procedure and analyzed by GC-MS. The data generated from the burnings was compiled into the same set as the data generated from the neat diesels so that PPMC and PCA could be applied to the entire data set. The potential for the association and discrimination of the burned diesels using these procedures was investigated.

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TABLE OF CONTENTS

LIST OF TABLES

****Images in this thesis are presented in color.**

LIST OF FIGURES

Chapter 1

Introduction

1.1 Arson

Arson is defined as the deliberate setting of a fire with the malicious intent to cause damage [1]. The United States Fire Administration (USFA) estimates that more than 30,000 intentional structural fires were set in 2006, which resulted in more than 300 civilian deaths [2]. These intentional fires were reported to have caused approximately $755 million in property damage. An estimated 20,000 vehicle fires were also set, which caused an additional $134 million in damages. Arson is a destructive and expensive crime, yet only a small number of cases ever result in an arrest or a conviction. The Federal Bureau of Investigation (FBI) reports that in 2002 only 16.5% of arson cases were closed [3]. This low rate of closure demonstrates the difficulties encountered in arson investigations and fire debris analysis, and indicates that research into the improvement of the methods in place is essential for advancements in this field.

1.2 Ignitable Liquids

Ignitable liquids are commonly used as accelerants in arson cases. The presence of an ignitable liquid, which is used to increase the rate and spread of a fire, may indicate that the fire was intentionally set. Common ignitable liquids frequently used as accelerants include petroleum distillates, such as gasoline, kerosene, and diesel fuel, and other hydrocarbon products, such as aromatic products and oxygenated solvents.

The American Society of Testing and Materials (ASTM) has developed a classification scheme for ignitable liquids based on chemical composition [4,5]. Nine classes have been differentiated for the characterization of ignitable liquids based on

composition: (1) gasoline-all brands, including gasohol, (2) petroleum distillates, (3) isoparaffinic products, (4) aromatic products, (5) naphthenic paraffinic products, (6) normal alkanes products, (7) de-aromatized distillates, (8) oxygenated solvents, and (9) others-miscellaneous. These classes are further divided into three subclasses based on the range of carbon content present in the liquid. The first subclass covers the light carbon range of C_4-C_9, with no components present above C_{11}. The medium carbon range includes C_8-C_{13} compounds, with none present below C_7 or above C_{14}. The heavy carbon range includes compounds at C_9 and above, with the typically observed range of C_9-C_{23}. It should be noted that these demarcations are not rigid, and that often samples are reported as "light to medium" or "medium to heavy" when the observed carbon range fits both profiles. The details of the ASTM classification scheme, including examples of common ignitable liquids that are representative of each class, can be found in Appendix A [4,5].

1.3 Analysis of Fire Debris

At a fire scene, ignitable liquid residues (ILRs) are most likely to be found in the area where the fire started, known as the origin. ILRs are also commonly found in pour patterns known as trailers, which occur when an ignitable liquid is poured in a constant stream from room to room in order to force the fire to spread throughout the entire structure. For evidence collection, the fire debris most likely to contain ILRs are those with porous surfaces, because the liquid may soak into them and thus be protected to some extent from the heat of the fire. Similar debris types that are not suspected to contain ILR are collected as control samples, which are necessary to prove that, if an ILR is detected, it is not a natural component or pyrolysis product of the debris matrix itself.

The laboratory analysis of fire debris encompasses the identification of both suspected neat liquids and ILRs extracted from burned and unburned substrates in the debris. The current protocols in place in forensic laboratories follow the ASTM standards that have been established and are maintained by the technical committee E30.01, which is the criminalistics subcommittee of the committee on forensic sciences [6]. ASTM standards are in place for both the analysis of ignitable liquids and the extraction of ILRs from debris.

In order for a suspected neat ignitable liquid to be analyzed, it is simply diluted in an acceptable solvent and then analyzed by gas chromatography-mass spectrometry (GC-MS). The analysis of fire debris for the presence of ILRs is similar to the analysis of a neat liquid. The difference arises in the need to extract the ILR from the debris in order for it to be analyzed by GC-MS. A variety of extraction techniques can be used, though each has its advantages and disadvantages. Five common extractions are listed by ASTM for the separation of ILRs from debris: steam distillation, solvent extraction, passive headspace concentration with activated charcoal, dynamic headspace concentration, and passive headspace concentration with solid-phase microextraction (SPME) [7-11]. Currently, the most frequently used extraction technique in crime labs is passive headspace concentration with activated charcoal strips, though solvent extractions are still valuable in some cases.

The ASTM standard E1412-07 details the procedure for the passive headspace extraction of ILRs from fire debris using activated charcoal [9]. The activated charcoal is suspended inside the submitted evidence container, and the container resealed. The container is placed in an oven and heated to a temperature of 50-80 °C for 2-24 hours.

The temperature and time heated is sample dependent, as higher temperatures and longer durations may be necessary to promote sufficient adsorption of less volatile compounds in the debris. After the adsorption step, the activated charcoal is washed with 50-1000 μL of an appropriate elution solvent, typically carbon disulfide, *n*-pentane, or diethyl ether. The eluate is collected and then analyzed by GC-MS. This procedure is capable of extracting ILRs across a wide range of concentrations with an extremely high level of sensitivity. It is considered a nondestructive technique for the extraction of ILRs from fire debris.

Solvent extractions, though less frequently used, can provide significant additional information in analyses when activated charcoal extractions are limited by volatility. Solvent extractions offer a more complete extraction that is representative of the entire range of compounds in a sample, whereas activated charcoal extractions are biased against less volatile compounds and those that are not selectively adsorbed onto the carbon strip. The ASTM standard E1386-00(2005) details the specifics of solvent extractions [8]. A suitable organic solvent, typically carbon disulfide, pentane, petroleum ether, or diethyl ether, is added to the debris. The solvent-debris mixture is thoroughly agitated for approximately one minute. The solvent is poured off and then filtered if particulates remain in the decantate. The extract is evaporated to approximately 1 mL and then analyzed by GC-MS. This technique is very sensitive, and is especially useful for the extraction of nonporous surfaces or when a small amount of sample needs to be extracted. The major disadvantage of solvent extraction is the concurrent extraction of interferences from the burned matrix. It must also be noted that some of the lighter classes of ignitable liquids may be lost in the evaporation phase of the procedure. The

ASTM standard suggests that, because solvent extraction is a destructive technique, it only be used in tandem with another extraction procedure. For example, if the results of an extraction with a charcoal strip indicate a heavy petroleum distillate, then a solvent extraction may also be performed in order to overcome the volatility bias in the charcoal strip extraction and to obtain a more representative chromatogram.

Both neat ignitable liquids and ILRs extracted from fire debris are analyzed by GC-MS per ASTM Standard E1618-06e1 [4]. The GC-MS is operated under conditions that are capable of adequately separating a test mixture consisting of common ignitable liquid constituents. The typical test mixture contains the even-numbered normal alkanes from C_8 to C_{20}, as well as toluene, *p*-xylene, *o*-ethyltoluene, *m*-ethyltoluene, and 1,2,4-trimethylbenzene. This test solution is usually prepared at a concentration of 0.005% (v/v) per component to ensure the sensitivity of the instrument [4,5].

Once a chromatogram has been obtained of neat ignitable liquid or extracted ILR, the pattern of its peaks, as well as the relative peak ratios, are used to determine whether or not it is consistent with a common ignitable liquid. In order for an ignitable liquid to be identified based on the aforementioned ASTM classification scheme, certain criteria in the chromatographic patterns must be met for each ignitable liquid class [4,5]. Information about the specific characteristics observed in the chromatographic profiles for each defined ASTM class can be found in Appendix A [4,5].

In addition to the chromatographic patterns, the mass spectral data are also used to identify the questioned sample. Extracted ion profiles (EIP) are generated for specific compound classes that are common to ignitable liquids. Table 1.1 lists the major ions that are used to create these summed profiles [12]. The patterns of the EIPs are also

Table 1.1 Major Ions Included in Extracted Ion Profiles for Ignitable Liquids [12]

Compound Class	Ion Mass-to-Charge (m/z) Ratio
Alkane	43, 57, 71, 85
Cycloalkane and alkene	55, 69
n-Alkylcyclohexane	82, 83
Aromatic	91, 105, 119; 92, 106, 120
Indane	117, 131; 118, 132
Alkylnaphthalene	128, 142, 156, 170
Alkylstyrene	104, 117, 118, 132, 146
Alkylanthracene	178, 192, 206
Alkylbiphenyl/acenaphthene	154, 168, 182, 196
Monoterpene	93, 136
Ketone	43, 58, 72, 86
Alcohol	31, 45

utilized in the identification of the questioned sample.

The method described above for the identification of ignitable liquids is subjective in nature, and is often based on the analyst's experience. The pattern recognition is not statistically based and frequently is not straightforward [4,5]. The questioned sample and reference samples used for comparison seldom correlate perfectly. In fact, the chromatograms of the questioned samples can be skewed due to weathering or insufficient recovery. Intense heat exposure from the fire can cause the loss of more volatile components at the beginning of the chromatogram. Interferences from the pyrolysis of substrate materials indigenous to the collected fire debris can create additional peaks in a questioned chromatographic profile. A fire debris analyst must be aware of these possible complications when making ignitable liquid identifications in order to prevent false positive identifications.

1.4 Current Literature Review

Fire debris analysis and ignitable liquid characterization is well represented in the literature [13-25]. Because the current method of ignitable liquid identification is subjective, research into more objective methods, such as association and discrimination by chemometric procedures, is essential for the advancement of fire debris analysis. Current research primarily discusses the utility of multivariate statistical methods in the association and discrimination of ignitable liquids [16-20, 23]. The importance of data processing prior to chemometric analysis is also discussed [26,27]. In addition to chemometrics, interferences and burning conditions have also been studied to determine their effects on fire debris analysis [28-32]. Although gasoline is the most commonly encountered ignitable liquid in arson cases [13] and most often discussed in the literature,

diesel fuel was selected as the ignitable liquid for this research project. Diesel was chosen because it is a complex petroleum distillate with a number of components that span the boiling point range, and it is less frequently discussed in the literature.

1.4.1 Statistical and Chemometric Analysis of Petroleum Distillates

Statistical comparisons of chromatograms produced from the analysis of various ignitable liquids have been limited to an evaluation of peak area ratios of specific components or to chemometric procedures performed on small sections of the chromatogram. Mann employed a method of comparing peak area ratios for eight components from the n-pentane to n-heptane region of the chromatogram to successfully discriminate gasoline samples [13]. Barnes *et al.* utilized a similar approach in which normalized peak area ratios of various aliphatic and aromatic constituents present in the headspace (*e.g.* substituted cycloalkanes, alkylbenzenes, and alkylnaphthalenes) were used to associate unevaporated gasoline samples to those from the same source that had been evaporated to 75% and 50% [14]. More recently, Sigman and co-workers described a statistical technique called covariance mapping in which gasoline samples could be distinguished based on distance metrics calculated between covariance matrices of replicates of both the same and different samples [15]. It should be noted that in a blind study of two unknown samples from a set of ten, one of the two was determined to be statistically different from its known source. It was suggested that evaporation of the sample between analyses could explain this Type I error. However, the presence of a Type I error, which is defined as a difference identified by the technique when one is not actually present, significantly limits the utility of the proposed identification methodology.

More advanced multivariate statistical techniques have also been utilized to associate and discriminate ignitable liquid samples. Sandercock and Du Pasquier used chemometric procedures such as linear discriminant analysis (LDA) and principal components analysis (PCA) on GC data collected using selected ion monitoring (SIM) for the C_0-C_2 naphthalene components in order to group similar gasoline samples based on grade, country of origin, and the season in which the sample was collected [16-17]. They employed similar methods to link evaporated samples to unevaporated samples [18]. Tan *et al.* utilized PCA and a soft independent model classification analogy (SIMCA) approach to differentiate GC-MS-SIM data of various ignitable liquids spiked onto wood and carpet as background matrices [19]. Successful classification was achieved for all ignitable liquids in the presence of wood and carpet using the developed SIMCA model. Doble *et al.* demonstrated the use of artificial neural network (ANN) algorithms to successfully classify 88 gasoline samples as either regular or premium grade based on the percent peak area of 44 compounds that were identified in all samples [20]. Similar ANN algorithms were also reported to distinguish the gasoline samples based on their season of collection with a 97% success rate.

While the majority of the forensic literature focuses on the identification and classification of gasoline samples as ignitable liquids, other more complex petroleum distillates such as diesel fuel have been discussed in the environmental science literature with respect to the association of samples collected from oil spills to their likely source. Environmental literature tends to focus on the use of unique classes of compounds in diesels in order to discriminate samples. In two recent studies, Wang *et al.* researched the ability of the sesquiterpane and diamondoid compound classes to potentially discriminate

diesel samples by analyzing more than 100 crude oils and refined products by GC-MS [21,22]. Diagnostic peak area ratios of several compounds from both the sesquiterpane and diamondoid classes were determined in an effort to identify the ratios that would provide the most discriminatory information. Ultimately these diagnostic ratios were effectively applied to a case in which the source of an oil spill was determined based on these two compound classes alone. The discriminatory potential of the sesquiterpane class was further investigated by Gaines *et al.* in which fourteen diesel samples were analyzed by GC-MS and extracted ion chromatograms (EIC) for 22 different characteristic compound classes were generated [23]. The peak ratios of several compounds within each of the 22 classes were determined and PCA was performed in order to select the ratios that generated maximum discrimination among samples. Results illustrated that full discrimination of all samples was possible with only nine peak ratios from the alkylbenzene, alkylphenanthrene, and sesquiterpane classes, and two samples from an actual oil spill were differentiated by the model developed.

More novel analytical methods have also been discussed in oil spill identification. Another study by Gaines *et al.* employed a qualitative and quantitative GC x GC approach to analyze a controlled oil spill [24]. By comparing two-dimensional ordered chromatograms, they observed that the patterns of alkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes, and anthracenes/phenanthrenes were useful in comparing the oil spill to one of its two potential sources. Quantitatively, four panels of integrated peak area ratios of the abovementioned compound classes were used to compare samples. Using both these methods a controlled oil spill was correctly matched to one of two potential sources. A study by Wang *et al.* showed a novel procedure for the visualization of GC-

MS data as a two-dimensional separation that is valuable in specific compound class separation when a nonfragmentation ionization technique is used [25]. This method was demonstrated on complex petroleum fractions, so that even compound classes at low abundances can be utilized for characterization.

1.4.2 Chromatographic Pre-processing

The need for pre-treatment of the chromatographic data prior to statistical and chemometric analysis has been more recently discussed in the literature, although it has yet to be applied specifically in a forensic science context [26]. Some pre-treatment processes, such as area normalization and mean-centering prior to PCA have long been demonstrated [27]. Another more significant pre-treatment is that of retention-time alignment of chromatograms to correct retention time drift anomalies caused by column degradation and random fluctuations in analysis conditions. Retention time alignment is an important step prior to PCA, since PCA maximizes the variance among a sample set. If the sample chromatograms contain multiple shifts in retention time, the PCA will focus on those differences in the samples instead of actual chemical variation.

Johnson *et al.* proposed a peak matching algorithm for the retention time alignment of GC peaks in order to reduce retention time shifts among several chromatograms [26]. This approach applies an estimation of the first derivative throughout the chromatograms and searches for zero crossings to identify peaks in a specified target chromatogram and the sample chromatograms. Peaks in the samples are matched to those in the target within a set window size and are then interpolated to include either more or less data points in the retention time axis so that the retention times of the peaks in the sample will be equal to those in the target. The authors demonstrated

the utility of this approach by analyzing a set of diesel samples by GC with a flame ionization detector (FID) and then subjecting them to the proposed algorithm followed by PCA. The unaligned set of 60 chromatograms exhibited differences in retention times up to 300 ms, but after alignment, the variation was only 17 ms with a relative standard deviation of 0.003%. PCA demonstrated that the alignment did not cause a decrease in chemical selectivity, but instead the resolution of clusters of different samples was shown to be greatly improved after alignment [26].

1.4.3 Burn Conditions and Matrix Interferences

The analysis of ILRs extracted from fire debris is not straightforward. In fact, the burning conditions and contributions from the burned matrix can hinder chemometric analysis. Artifacts present in the chromatogram from sample weathering or matrix interferences may cause samples that are actually similar to be difficult to associate because of the extraneous components. These issues have been moderately discussed in the literature, though most studies only look at the matrices alone without any ignitable liquid present, much less an ignitable liquid that has been burned as would be the case in an actual arson situation [28-32].

Bertsch examined potential interferences from carpet samples in the identification of ILRs, specifically gasoline, from fire debris [28]. It was observed that when carpets and carpet paddings were burned that some amounts of alkylbenzenes and naphthalenes were produced. These same compounds are typically used as markers in the identification of gasoline. It was determined, however, that by observing EICs of the C_2-C_5 alkylbenzenes (m/z 106, 120, 134, and 148) and the methylnaphthalene isomers (m/z 142), the relative amounts of these compounds observed in a gasoline versus that

produced by the pyrolysis of carpet is distinguishable. It was noted, however, that when the carpet has been freshly manufactured some remnants of petroleum-based products used in the manufacturing process may still be detectable. In addition to these remnants, carpets treated with petroleum-based water-proofing agents or insecticides may also produce a gasoline-like chromatogram. The use of EICs in this case is not beneficial for the identification of gasoline because the petroleum product is inherent to the carpet itself. In a similar study, Cavanagh *et al.* examined carpets and mats from cars of unknown history, and a small percentage of these carpets exhibited a chromatographic profile similar to that of evaporated gasoline [29]. The authors suggested that inherent interferences from car carpets are uncommon, which would increase the evidentiary value of the presence of a more concentrated ILR sample or one that does not compare with an evaporated profile.

Lentini *et al.* presented a study in which several commonly encountered materials were shown to produce petroleum-like chromatograms [30]. Several samples of different matrix types were analyzed using passive headspace concentration followed by GC-MS. The matrix types analyzed included clothing, shoes, household products, building materials, paper products, cardboard, and adhesives. Many of the substrates examined exhibited TICs or EIPs very similar to those of ignitable liquids, though patterns consistent with gasoline were much less frequently observed than those of medium of heavy petroleum distillates. It was concluded that, because of these potential sources of interference that are likely due to the regular use of petroleum products in the manufacturing, cleaning, and treating processes, control samples are crucial as a reference in fire debris analysis. In another similar study, Almirall and Furton analyzed

common household products that had been burned in controlled conditions and also reported consistency in composition with ignitable liquids [31]. They determined the five most frequently encountered compounds in these substrates that are also observed in ignitable liquids are toluene, styrene, naphthalene, benzaldehyde, and ethylbenzene. In addition, Almirall and Furton analyzed several of the same samples using pyrolysis GC-MS to characterize the products formed during burning. These pyrolysis products, most frequently toluene, naphthalene, styrene, and ethylbenzene, may serve as another source of interference in the identification of ignitable liquids extracted from fire debris.

Borusiewicz *et al.* studied several factors that may influence the collection and detection of ILRs, and, unlike the previous studies mentioned, actually included the spiking of ignitable liquids onto the matrices being analyzed [32]. By reproducing burn conditions and visually comparing chromatograms, the authors were able to examine how the ignitable liquid type, burned matrix type, burn time, and air availability affect the ability to detect ILRs. They concluded that the material being burned (*e.g.* wood, carpet, etc.) is the most significant factor in ILR analysis. The other parameters were determined to be less significant, even when compared to random variables in fire debris analysis that are difficult to replicate in a laboratory setting, such as ignitable liquid dispersion or the arrangement of the material when burned. The disadvantage of this study is that the ignitable liquids analyzed were not actually burned; instead, they were only spiked onto already burned matrices.

1.5 Research Objectives

In the preliminary work of this project, conducted throughout the summer and fall of 2006, neat diesels were analyzed by GC-MS and characterized using PPMC and PCA

[33]. 25 diesels from eight different brands of service stations were collected for analysis and characterization. In addition to the TICs, EICs were generated for representative compounds of both aliphatic (m/z 57) and aromatic (m/z 91 and m/z 141) constituents present in the diesel samples. PPMC coefficients were generally observed to be higher between diesels from the same brand and lower between those from different brands. A wider array of PPMC coefficients were observed in the EICs, especially for m/z 91, which suggests that the aromatic composition of the diesel may be the source of the variance between those diesel samples. PCA scores plots typically showed four diesel sample clusters, three that contained only samples from one brand and one with the remaining samples. This trend was generally observed for both the TIC and EIC data. The PCA loadings plots, which demonstrate the contribution of each component to the variance in the data set, suggested that the relative aliphatic and aromatic composition, similar to that observed by PPMC calculations, was the most significant source of variation among the samples.

The fundamental objective of this research project is to expand on the previous work and study the possibility of linking ignitable liquid residues extracted from fire debris to a neat liquid sample. Again, diesel fuel was selected as the ignitable liquid for this project because it is more chemically complex than other ignitable liquids such as gasoline, and because it is less frequently discussed in the literature. Basic statistical and more advanced chemometric procedures, such as PPMC coefficients and PCA, are implemented to associate and discriminate both neat diesels and those that have been extracted from burned debris based on their chemical composition. Data pre-treatment issues, which include chromatographic alignment and normalization, are also considered.

This project expands on the current research described in the literature by focusing primarily on the ability to link an unburned diesel sample to a diesel sample that has been extracted from burned debris. This project examines data from the entire chromatogram instead of just peak ratios or sections of the chromatogram as reported in the literature. Using the entire chromatogram may increase discrimination capability, and no information needs to be known or assumed about the samples in question. EIPs of several potential characteristic compound classes (*e.g.* aliphatics, aromatics, polynuclear aromatics, and indanes) are also used for comparison. Again, this project implements the entire EIP to further enhance discrimination. The increased chemical information from the full TICs and EIPs may potentially show more significant association and dissociation of diesel based on chemical composition in chemometric procedures. The chemometric procedures may overcome the changes produced in the diesel sample due to burning as well as matrix interference contributions so that a burned sample can be accurately associated with its neat counterpart, which minimizes the risk of false positive ILR identifications. This research, which is applicable to almost any petroleum product with potential as an ignitable liquid, serves as the groundwork for future projects, and could ultimately conclude with scientific validation for use in a forensic laboratory setting.

Chapter 2

Analytical and Chemometric Theory

2.1 Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) is a well developed analytical technique that has become commonplace in forensic laboratories because of its wide application range. The combination of chromatographic and mass spectral results offers a multidimensional analytical tool. It is commonly used in forensic laboratories for drug analysis, toxicology, environmental contamination, and explosives detection. It is also the standard technique used for ignitable liquid identification and fire debris analysis. In fact, as previously described in Chapter 1, a standard method has been developed by ASTM for the specific use of GC-MS in the analysis of ignitable liquid residues in fire debris extracts [4].

Chromatography is a technique in which separations of mixtures are driven by interactions of individual components in the mixture with a mobile and a stationary phase. In gas chromatography, the mobile phase is an inert carrier gas, typically helium or nitrogen. A GC system consists of several individual components: a heated injection port, through which the sample is introduced, a column housed in a temperature regulated oven, where the separation takes place, and a detector. Several different types of columns and detectors are available for use based on the sample and the type of separation required. In GC-MS, the typical column is a capillary column with the stationary phase coated on the inner walls, and the mass spectrometer serves as the detector. In order to analyze a sample by GC-MS, it must be volatile and thermally stable.

In a GC-MS system, the sample must be introduced in the vapor phase. Liquid injections, however, are commonly performed, because the injection port is sufficiently heated (250 °C and above) to immediately vaporize the sample. The mobile phase constantly flows through the system and sweeps the vaporized analytes onto the column. The column, as mentioned before, contains the chromatographic stationary phase to cause separation. The stationary phase is usually coated directly on the interior surface of the capillary column, though it can also be coated onto particles that are used to pack the column. The affinity of the analyte for this stationary phase dictates its retention on the column. For example, if a component has a significant affinity for the stationary phase (*e.g.* a polar component with a polar stationary phase), it will interact more with it than a component with a lesser affinity (*e.g.* a non-polar component with a polar stationary phase). The component with a higher affinity will be more retained and will elute later than the component with the lesser affinity. The parameters of the column, such as length, diameter, and stationary phase thickness, as well as the composition of the stationary phase itself, have an effect on retention and ultimately the quality of the separation.

The positioning of the column in a temperature regulated oven allows for it to be heated to facilitate analyte separation. In an isothermal analysis, the oven is held at a constant temperature throughout the course of the run. This temperature is typically at or just above the boiling point of the sample to be analyzed. For samples that contain components with a broad range of boiling points, a temperature programmed analysis provides better resolution, quicker analysis time, and minimal band broadening in comparison to isothermal conditions. In a temperature program, the oven is held at some

initial temperature in order to initiate the separation as well as to prevent condensation of the analytes on the top of the column. The temperature is then ramped over the course of time to a final temperature. The rate of the ramp is dependent on the sample. A slower ramp rate is often used when components that have similar boiling points need to be separated, such as in a complex mixture like diesel. Faster ramp rates, however, provide quicker analysis times, thus ramp rates are often selected to provide sufficient resolution in the minimal amount of time. The oven is then held at the final temperature to ensure complete analyte elution.

The column passes through a heated transfer line into the ionization source of the mass spectrometer detector. The transfer line must be maintained at a high temperature, typically 300 °C, in order to prevent condensation of the separated analytes during transfer into the director. From the transfer line, the analytes are introduced directly into the ionization source where they are ionized and fragmented. Several types of ionization sources are available, each with its advantages and disadvantages. Electron impact (EI) ionization is the most common in most bench-top GC-MS instruments used in forensic laboratories for fire debris analysis. In EI, a filament with electric current running through it is heated in order to produce high-energy electrons (70 eV). These electrons interact with the vaporized analyte molecules to produce molecular ions that are fragmented through further collisions. These positive molecular and fragment ions are then transported by a series of focusing lenses into the mass analyzer, where they are separated based on their individual mass-to-charge (m/z) ratio.

As with ionization sources, several types of mass analyzers are available for use, but the most common in bench-top instruments is the quadrupole mass analyzer. The

quadrupole consists of four parallel conducting rods, with one pair connected to the negative terminal of a DC source and the other pair connected to the positive end. Each pair is also connected to a radio frequency (RF) AC source. These four rods define a cylindrical region through which the ions travel. Under the influence of the electric field, the positive ions are attracted to the negatively charged rods. As the ion begins to move toward the negative rod, the potentials on the rods are switched, and the ion moves toward the opposite rod that is now negative. As the potential is varied, the ion travels in an oscillating pathway through the quadrupole and on to the detector. At a given DC/RF ratio, only ions of a narrow m/z value will travel an oscillation path that allows them to pass through the region defined by the rods without hitting the rods. Ions of other m/z values will travel a wider path that will cause them to come in contact with the charged rods, become neutralized, and therefore not be detected. A full mass scan is obtained by increasing the DC and RF potentials while still maintaining a constant ratio between the two. As the ions pass through the quadrupole, they are directed to a transducer, typically a continuous conversion dynode. The positive ions contact the highly negatively charged conversion plate, which causes the release of secondary particles, of which electrons are included. These electrons then enter the continuous dynode electron multiplier, where they strike the multiplier plates, which are coated with a substance the readily emits secondary electrons. This release of electrons caused by the contact with the plates results in a cascade of electrons that reach the end of the multiplier where they are detected.

GC-MS results are two-fold. The retention time of a component, as well as its mass spectrum, are used in making comparisons among samples. In a conventional GC-

MS analysis, the entire mass range is scanned during detection and a total ion chromatogram (TIC) is generated. The TIC is a plot of intensities of m/z values in each scan versus time. From this TIC, a specific m/z ratio can be selected as a filter so that only the signal from that ion is retained while all signal from all other ions is eliminated. The result is an extracted ion chromatogram (EIC) in which the abundance for a particular ion is plotted against retention time. EICs can be useful to reduce highly complex and convoluted samples to a more manageable format for interpretation. In fire debris analysis, EICs are beneficial to reduce a petroleum distillate, which is a very complex mixture of many components, to only those components of a specific compound class, such as aliphatics or aromatics. The amount of aliphatic and aromatic components present in an ignitable liquid is valuable information for ignitable liquid classification. In fire debris analysis, several individual EICs are summed to generate an extracted ion profile (EIP) of multiple representative ions of a characteristic compound class. These EIPs are at higher abundance levels and contain more characteristic features than EICs alone.

2.2 Data Pre-treatment

Data pre-treatment is necessary prior to the application of chemometric procedures in order to correct for any variation among the diesels not actually due to differences in chemical composition. For example, minor shifts in retention time can occur between sample injections due to instrumental drift in the GC-MS. Retention time alignment procedures can correct for these nominal variations in retention time. Another source of variation among the samples includes slight differences in injection volume. A normalization process can correct for these slight differences. Data pre-treatment

procedures are essential in order to ensure accurate results from the PPMC coefficients and PCA.

2.2.1 Retention Time Alignment

The first data pre-treatment step that must be taken after the raw data is collected is a retention time alignment. The alignment is necessary to account for normal instrumental drift, such as slight changes in temperature, pressure, and flow rate, from run to run. Retention time shifts can also be caused by the natural aging process of the column, which degrades over the course of several runs. A retention time alignment algorithm can correct for these inevitable sources of retention time drift. The algorithm used in this work was developed specifically for diesels and is available in the literature [26]. Figure 2.1, which highlights the decane peak for Diesels 1-5, illustrates the effect of the application of the retention time alignment algorithm to the raw chromatographic data. The decane peak in Diesel 2 is severely shifted when compared to the other diesels, but the algorithm is capable of correcting for that shift.

In the algorithm a representative target chromatogram is chosen by the user from the sample set to be aligned. The first algorithm function is to perform a baseline correction on the target and sample chromatograms. The baseline correction factor is determined by a linear regression through the first few points and the last few points of the chromatograms. This correction is applied to account for minor changes in the baseline from run to run, though it is contained in a sub-routine in the algorithm and is easily edited or even removed if deemed unnecessary. The algorithm then cycles through each chromatogram in turn and estimates the first derivative of the chromatogram by calculating the difference in signal strength between consecutive data points. Once this

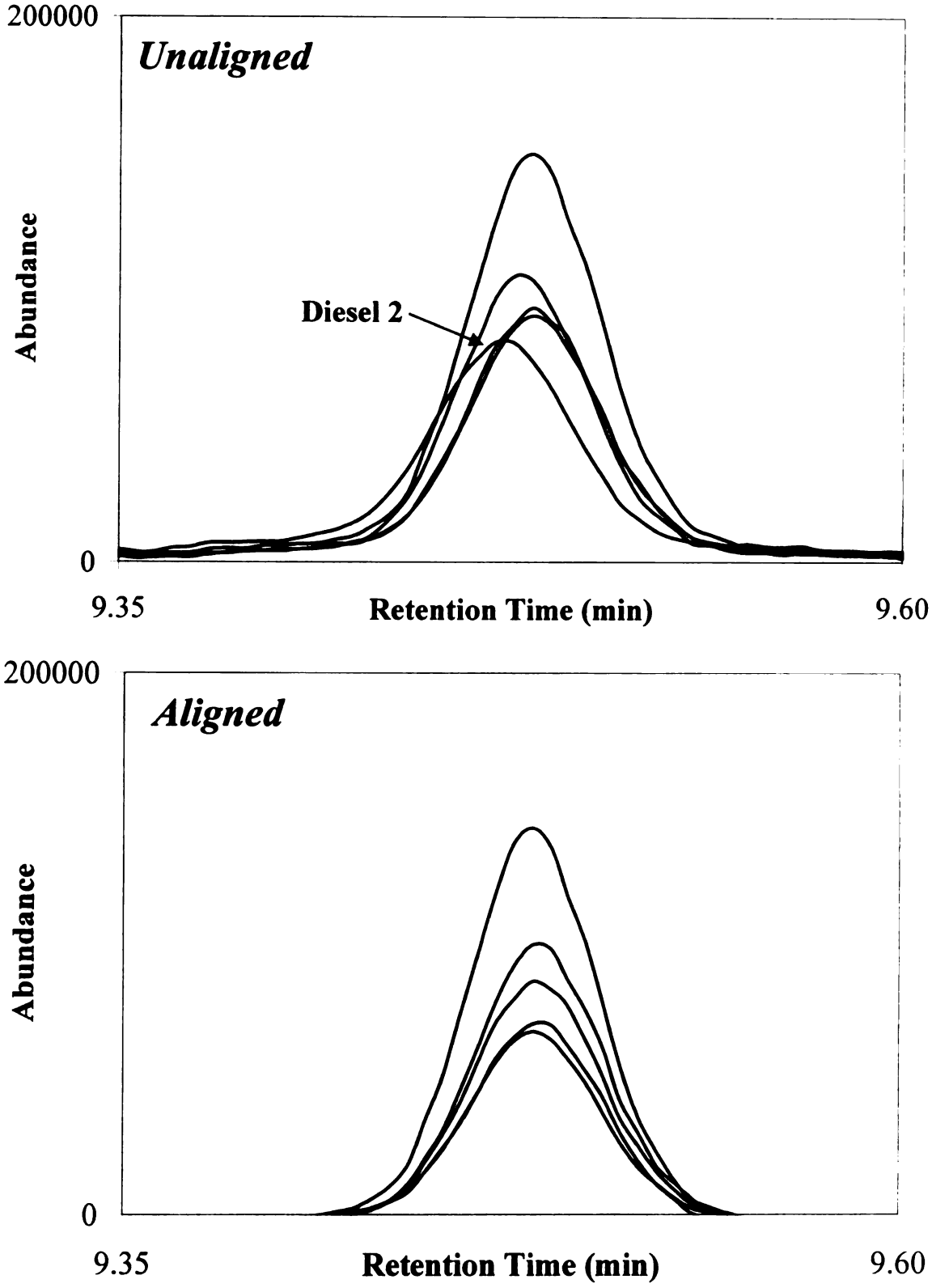

Figure 2.1 The Effects of a Retention Time Alignment Algorithm on the Decane Peak of Diesels 1-5

difference exceeds a threshold for baseline noise defined by the user, the data points are considered to be the leading edge of a chromatographic peak. The algorithm then searches for a zero crossing, or a change in sign, within this first derivative estimation, which indicates the apex and tailing edge of a chromatographic peak. The algorithm then interpolates the subsequent retention time at which the first derivative is equal to zero, rounds that retention time to the nearest integer value, and then adds that retention time to a list being generated for that chromatogram. Once the retention time tables for each chromatogram have been compiled, the algorithm compares the peaks present in each sample with the peaks identified in the target chromatogram. If the sample chromatogram contains a peak within a user-defined window size to that of the target, then it is considered a match and the retention time axis will be interpolated to include more or fewer data points so that the sample peak has the same retention time as the target peak and the peaks align. If the target chromatogram contains a peak that the sample chromatogram does not, or vice versa, those peaks are not considered in the retention time axis interpolation, which allows the alignment to accommodate samples that contain varying numbers of peaks.

Prior to implementation, however, certain user-specified parameters of the alignment algorithm need to be investigated in order to ensure optimal alignment. The selection of the target chromatogram must be done carefully so that it contains as many peaks present in the chromatograms to be aligned as possible. It is also important that the peaks in the target chromatogram are relatively centered in terms of retention time and peak symmetry in comparison to the peaks from the sample chromatograms. A poor target selection will lead to a greater propensity for misalignments. Another factor

defined by the user that must be considered is the baseline noise threshold for peak identification. The noise of the chromatogram is determined from the first several data points in the chromatogram by default. However, because diesel chromatograms contain features within those first points, in this research the algorithm was amended to calculate the noise from the last several points in the chromatogram where a baseline was discernible. The standard threshold for determining the presence of a peak is five times the standard deviation of the calculated noise. The last user-defined variable that requires investigation is the window size. This last parameter dictates the magnitude of retention time shift of a peak in a sample chromatogram that is still determined a match to the same peak in the target chromatogram. Ideally, the window size, which the algorithm defaults as five, is large enough to account for normal retention time drift, but smaller than the average distance between adjacent peaks. A brief examination of these parameters can lead to fewer errors and improved alignments.

Even after optimization of these variables, the alignment algorithm is not devoid of limitations. Peaks with small signal-to-noise ratios are often not identified because they still fall below the optimal baseline noise threshold. These smaller peaks also tend to be noisier, which can result in the determination of multiple zero crossings and leads to peak misidentifications. Another limitation of the alignment algorithm is that the peak identification method of first derivative estimations is entirely dependent on the scan rate of the mass spectrometer. Smaller peaks are often overlooked by the algorithm's peak finding function when the scan rate is too rapid because the first derivative is not substantial enough to exceed the noise threshold. The alignment algorithm also lacks any method for the determination and alignment of shouldered peaks. Their identification

depends on the size of the shoulder in comparison to its parent peak, so that some shoulders are well aligned while others are not. Despite these limitations, the alignment algorithm has been demonstrated in the literature to be adequate for GC peak alignment of diesel samples [26]. The user, however, must be aware of the consequences of these limitations not only on the alignment itself, but on the ensuing chemometric analyses as well.

2.2.2 Area Normalization

In addition to retention time alignment, other pre-treatment steps are necessary to minimize sources of variation in the chemometric analyses introduced by the analytical technique or injection method. Minimizing artificial variation ensures that the results of Pearson product moment correlation (PPMC) coefficients and principal components analysis (PCA) are based on the true sample variation. Normalization is performed in order to account for minor differences in injection volume from run to run. In a basic normalization process, each chromatographic peak is ratioed to a reference that is present at a consistent concentration throughout every analysis. In many cases, the reference peak is a purposely added component known as an internal standard that is not inherent to the sample being analyzed. However, because diesels are complex and contain numerous components that cover a broad range of boiling points, the choice of an internal standard that would not co-elute with a native component is difficult. Therefore in this research, an area normalization process was used instead. In this method, the areas of all peaks present in a chromatogram are summed, and the individual peak areas are then divided by the total area. In this research, however, the entire chromatogram is analyzed, not just the areas of each peak. In order to area normalize the individual data points of the full

chromatogram, the total area underneath the chromatographic curve is calculated to serve as the reference. The individual data points are then divided by the total area. The data points are then multiplied by an average of the total areas of all sample chromatograms in the data set in order to return the chromatograms to the original order of magnitude so as to maintain discernible features for further data analysis.

Figure 2.2, which shows the same decane peak of the five diesels as before, demonstrates the results of the area normalization process. In the aligned data only, it appears that little similarity exists among the five diesels in the concentration of decane present. However, once the data is normalized, clear associations can be made for Diesels 3 and 4 as well as for Diesels 1, 2, and 5. These two sets are easily differentiated based on the concentration of decane present.

2.2.3 Mean-Centering

Another pre-treatment step, mean-centering, is performed specifically in preparation for PCA. In this process, the mean of an individual variable (in this case, the abundance level at a single retention time) is calculated across the entire data set. This mean is then subtracted from each value so that the resultant sum across the sample set equals zero. Figure 2.3 shows the same decane peak of the five diesels as before, but now the data has been aligned, normalized, and mean-centered. The same diesels are associated as before, only in the mean-centered plot, Diesels 1, 2, and 5, which were lower in decane concentration, exhibit a negative peak. Diesels 3 and 4, on the other hand, remain positive. It should be noted that the two positive peaks are greater in magnitude than the three negative peaks, a characteristic that is observed because the means have been mathematically forced to sum to zero.

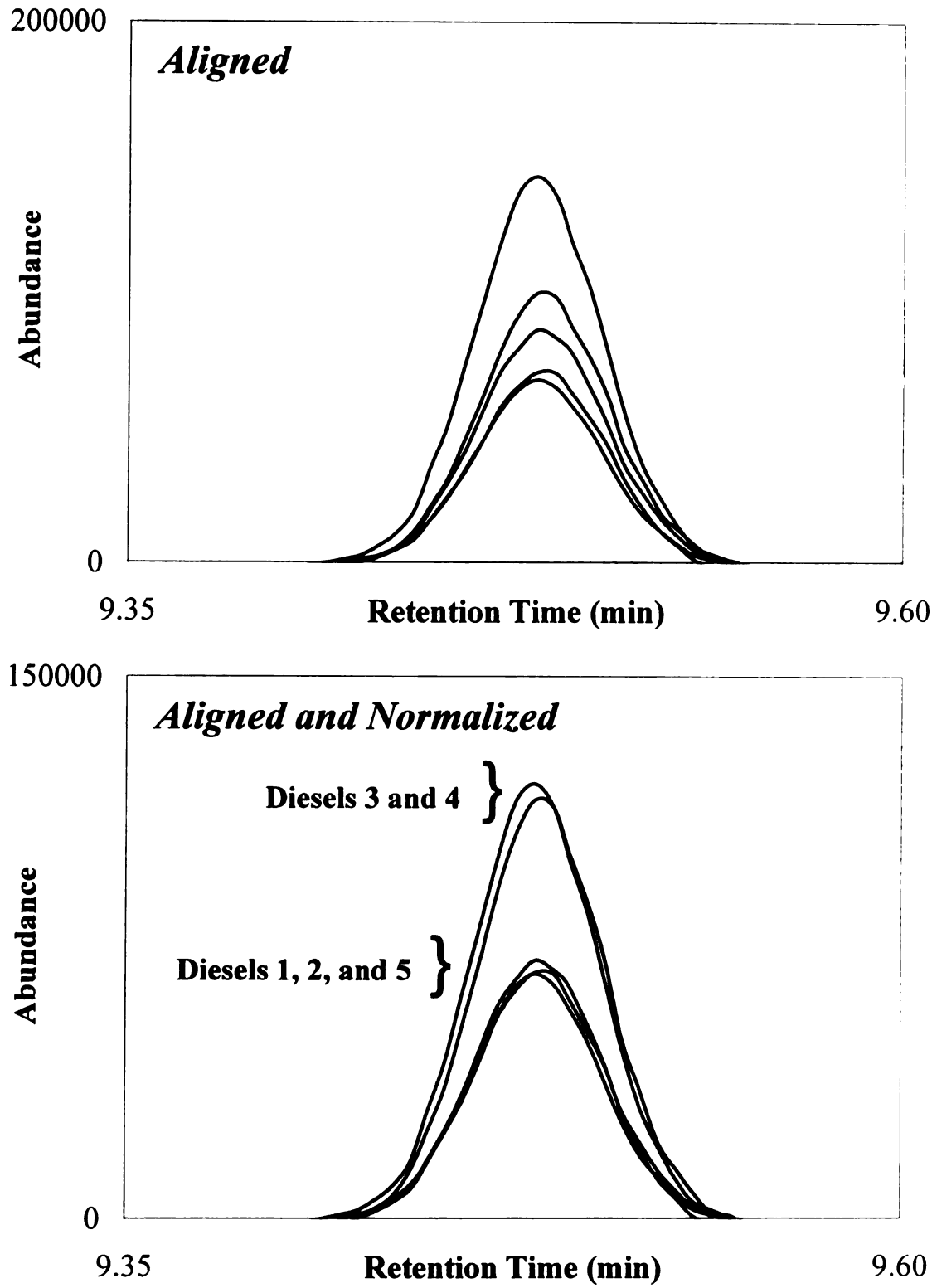

Figure 2.2 The Effects of Area Normalization on the Decane Peak of Diesels 1-5

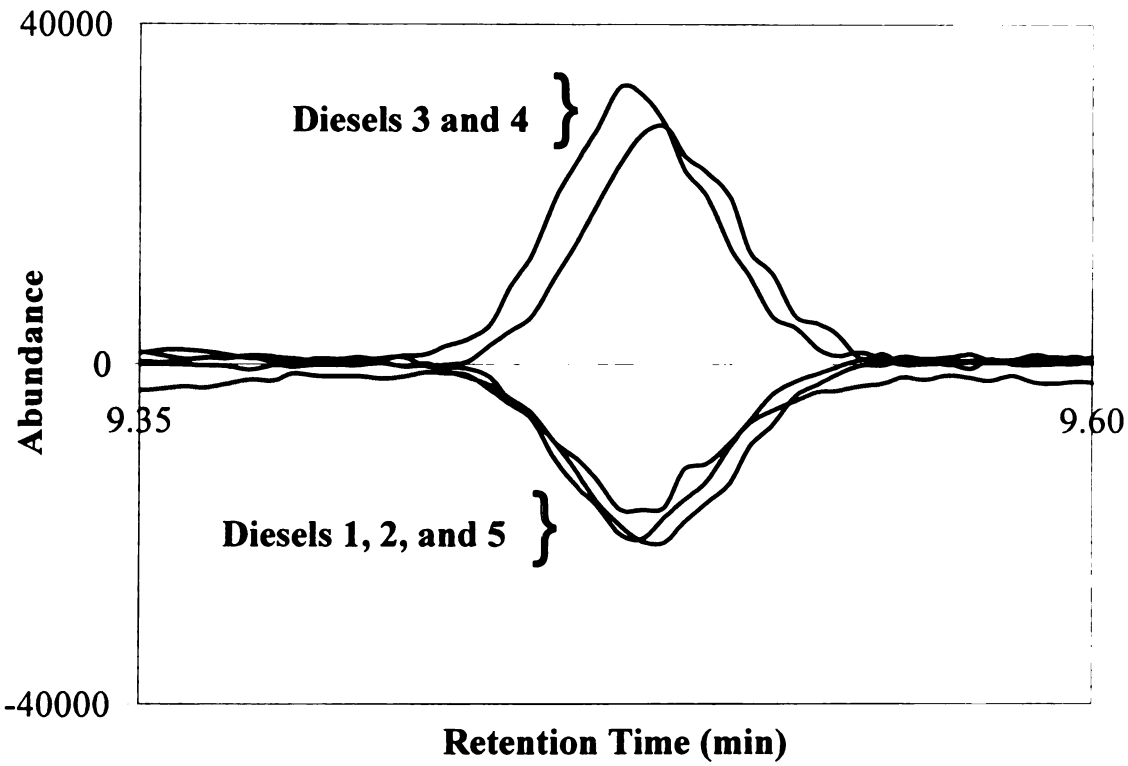

Figure 2.3 The Application of Mean-Centering to the Decane Peak of Diesels 1-5

Mean-centering is an important step prior to PCA to ensure that the maximum variance described by the principal components selected does not contain any deviations from the mean. Oftentimes when PCA is performed on data that has not been mean-centered, the primary principal component reflects how the samples deviate from the mean, not necessarily how they inherently vary. Upon mean-centering, the variance becomes centered around the origin so the principal components are allowed to describe actual sources of variation among the samples.

2.3 Pearson Product Moment Correlation Coefficients

The PPMC coefficient (*r*) indicates the degree of linear correlation between two samples. The correlation coefficient is calculated by dividing the covariance between the two samples by the product of each sample's standard deviation as shown in Equation 2.1:

$$r = \frac{\sum (X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\sum (X_i - \overline{X})^2}\sqrt{\sum (Y_i - \overline{Y})^2}} \qquad \textbf{Equation 2.1}$$

Values for *r* range between -1 and 1, where a correlation of 1 indicates a perfect positive linear relationship and a correlation of -1 indicates a perfect negative linear relationship. It has been suggested that correlation coefficients between 0.8 and 1 indicate a strong correlation between samples, while coefficients between 0.5 and 0.8 indicate a medium correlation. Coefficients less than 0.5 imply a weak correlation [34]. Correlation coefficients close to zero signify a lack of any correlation.

To assess the correlation between two diesel samples, coefficients are calculated as in Equation 2.1, where the *X* variables denote abundances at individual retention times for one diesel, and the *Y* variables correspond to abundances at the respective retention

times for the other diesel. In order to determine the strength of association between two diesels, the standard convention mentioned above is not applicable because of the level of inherent similarity of the samples being compared. The conventional model relates to samples that range significantly in their chemical composition. Diesels, however, are very similar in their basic composition, so their correlation coefficients would be expected to be closer to unity. Therefore, although differences in correlation coefficients between diesels will be smaller, these differences may still be significant.

A more appropriate guideline for samples like diesel that are already so similar is the range of coefficients between several replicate analyses of the same sample. Replicate coefficients, which represent the highest possible level of similarity, should be close to unity. If correlation coefficients between samples that are not replicates fall within the same range as the replicates, then those samples must be considered very similar. Diesels with correlations outside that range can be considered less similar due to differences in chemical composition. With the application of this guideline, PPMC coefficients are useful in assessing the association and discrimination of diesels based on chemical composition.

Another application of PPMC coefficients is method precision. As previously mentioned, replicate analyses should result in correlation coefficients of unity if the instrumental technique and manual injection procedure are repeatable. Because of random instrumental and analyst variations, perfect correlation coefficients are unlikely; however, coefficients very close to one should be attainable between replicate analyses. Therefore, average correlation coefficients of replicates can serve as an indicator of how precise the instrument and the manual injection process are.

2.4 Principal Components Analysis

PCA is a multivariate statistical technique most commonly used to reduce larger data sets to dimensions that can be easily visualized by standard procedures while still retaining the most significant information. PCA, on the most basic level, determines the sources of maximum variation among samples in a data set and clusters the samples based on their relative contribution to these sources of variation. It is a clustering technique that is capable of associating and discriminating samples based on how they are correlated.

PCA consists of several steps of complex matrix mathematics. The first step is to generate the covariance matrix, which consists of covariance calculations between all dimensional pairs in the data set. The covariance between a pair is calculated by Equation 2.2:

$$\mathrm{cov}(X,Y) = \frac{\sum (X_i - \overline{X})(Y_i - \overline{Y})}{(n-1)} \qquad \textbf{Equation 2.2}$$

The covariance matrix for a data set of n dimensions contains $n!/(n\text{-}2)!*2$ different covariance values, as well as commutative repeats [cov(X,Y) = cov(Y,X)] and covariance identities [cov(X,X)], which are equal to the variance of that variable [35]. These commutative repeats make the covariance matrix symmetric about the forward diagonal.

The next step in PCA is to calculate the eigenvectors and eigenvalues of the covariance matrix. Eigenvectors are derived from the basic properties of transformation matrices. A vector that, when multiplied by a square matrix, results in a reflection of itself is considered an eigenvector of that matrix. Any multiple of that vector is also considered an eigenvector because the directionality of the vector is not affected, only the length. In simpler terms, an eigenvector α is a vector that satisfies the following

relationship with a square matrix A: $\alpha * A = \lambda * \alpha$, where λ is a nonzero number known as the eigenvalue. In PCA of a multidimensional data set, computerized iterative algorithms are often employed to calculate all the eigenvectors and their associated eigenvalues of a covariance matrix. The eigenvectors are then ranked in descending order by their respective eigenvalue. The maximum eigenvalue corresponds to the most significant eigenvector. It should be noted that eigenvectors are orthogonal to one another, and that *n* eigenvectors are calculated for a matrix of *n* x *n* dimensions.

For PCA, the eigenvector with the largest eigenvalue is the first principal component (PC1). This primary eigenvector can be thought of as the axis on which the original data can be projected that results in the maximum amount of spread among the samples in the data set. Additional PCs, positioned orthogonally in the sample space to the previous PC, describe lesser amounts of variation corresponding to the magnitude of their eigenvalues. The amount of variation afforded by each PC is represented as a percentage of its eigenvalue to the sum of all eigenvalues. Often, only two to three PCs are needed to describe 85-90% of the variance among the data [27]. The dimensional reduction property of PCA is reflected in the significant eigenvalues. If a complex data set of many dimensions can be accurately described by only two or three dimensions, which are capable of being plotted and visually observed, the analysis of that data set becomes much easier by conventional methods.

Once the eigenvectors and eigenvalues have been determined, they are utilized to calculate scores for each sample. Scores are calculated for each sample by a simple matrix multiplication of the original data (in columns) by the eigenvectors (in rows). This multiplication results in a single score for each sample for each principal

component. A scores plot usually consists of an x-y scatterplot of the PC1 score versus the PC2 score for each sample. Three-dimensional plots of the scores for the first three PCs are also frequently used. In these scores plots, the samples will cluster based on how they are each affected by the eigenvectors selected. For diesels, the eigenvectors correspond to individual chemical components that are the most variable among them. Therefore, the scores plots cluster diesels based their similarities and differences in chemical composition. A plot of the individual eigenvectors, known as a loadings plot, indicates those components that contribute the most to the variance. If a component loads high, then it contributes more significantly to the score of a sample than other components do.

Although clustering patterns observed in scores plots can be used for sample association, PCA is an unsupervised technique, because the method is not guided by or modeled after a known training set. Instead, PCA clusters samples in a data set solely on how those particular samples vary. As samples are added or removed, the clustering results may change. For this reason, empirical classification by PCA is difficult; instead, it is more useful to discuss how the samples fall into the clustering patterns by degrees of association with and discrimination from one another.

Chapter 3

Association and Discrimination of Neat Diesels Using PPMC Coefficients and PCA

3.1 Introduction

The fundamental objective of this research is to investigate the potential of linking ILRs extracted from fire debris to the corresponding neat liquid sample using chemometric procedures, specifically PPMC coefficients and PCA. The initial step, however, is to demonstrate that similar neat ignitable liquids, diesel fuel samples from different service stations in this case, can be associated and discriminated based on differences in their chemical composition. This preliminary work is essential in order to show that PPMC and PCA are capable of distinguishing diesel samples that are known to be very similar in their basic chemical composition. If the neat diesels cannot be differentiated, then burned diesels will be nearly impossible to discriminate, because they will have lost the more volatile components, and hence some discriminatory information, during the burning process.

Although diesels have a similar basic composition, some amount of variation is introduced through the refining process. Diesel is a heavy distillate fraction collected from the refining of crude oil. Oil refining is a multistep process that includes a temperature-based fractional distillation, several chemical processing steps (thermal or catalytic cracking, and hydrocarbon unification or alteration), and multiple purification and product blending phases [36]. Refineries may also include various additives in their final product blends to improve their quality and performance. Refineries differ in how they complete these processes to produce their final diesel fuel product, which adds some amount of variation to a distillate fraction that is generally similar in composition.

The differences in the refining process allow for potential association and discrimination of diesels based on how they were produced. However, it must also be noted that the refining process itself is variable, so that even products from the same refinery may vary. In addition to random variations in the refining process, diesel fuel products must be transported to a distributor and then finally a service station for purchase by the consumer. While some service station brands such as Marathon refine their own oil to sell, other brands such as Speedway or Meijer purchase their products from a regional distributor [37]. Some stations have long-term contracts with distributors so that they always receive similar products, while others purchase their products on a need basis from the most cost efficient distributor. Therefore, it is impossible to generate a database of diesel samples from different service stations because of these constant changes. This variation must be considered in the interpretation of the PPMC and PCA results for the association and discrimination of diesel samples.

In order to examine a neat diesel data set, diesel samples were collected, analyzed by GC-MS, and subjected to both PPMC and PCA in order to assess the degree of association and discrimination achieved among them.

3.2 Sample Collection and Analysis

Ten diesel samples were collected from various service stations located within the surrounding area of Lansing, Michigan. Table 3.1 lists the samples, which were numbered consecutively, and the details of their collection. It should be noted that five brands of service station (Sunoco, Speedway, Meijer, Marathon, and Mobil) are represented in the sample set. Diesel samples were collected from two different locations of each of the five brands in order to have a representative but diverse data set.

Table 3.1 Diesel Collection Log

Sample	Service Station	Location	Date of Collection	Color at Time of Collection
Diesel 1	Sunoco	2139 Haslett Road	05/31/07	pale yellow
Diesel 2	Sunoco	3000 Dunckel Road	06/06/07	pale yellow
Diesel 3	Meijer	550 Hull Road	06/07/07	fluorescent yellow
Diesel 4	Meijer	2055 West Grand River Avenue	06/11/07	fluorescent yellow
Diesel 5	Mobil	1500 Haslett Road	06/12/07	fluorescent yellow
Diesel 6	Speedway	16819 Marsh Road	06/13/07	fluorescent yellow
Diesel 7	Mobil	2704 Lake Lansing Road	06/15/07	fluorescent yellow
Diesel 8	Marathon	3010 West Lake Lansing Road	06/18/07	fluorescent yellow
Diesel 9	Marathon	401 South Pennsylvania Avenue	06/19/07	fluorescent yellow
Diesel 10	Speedway	1659 Grand River Avenue	06/20/07	fluorescent yellow

Approximately one-half gallon of diesel was collected from each station in a five gallon yellow diesel container (Wedco, Willowbrook, IL). The containers were cleaned with hexane (reagent grade, Mallinckrodt, Phillipsburg, NJ) between sample collections.

After collection, the diesels were brought to the laboratory, transferred to previously acid washed 250 mL amber bottles, and stored in a refrigerator. Immediately prior to analysis, the diesels were diluted 200:1 with dichloromethane (CH_2Cl_2, spectrophotometric grade, Sigma-Aldrich, St. Louis, MO) in clear glass vials (Kimble Chase, Vineland, NJ). One μL of the sample was injected into the GC-MS running the Diesel.M method, which employs the following temperature program: initial temperature 50 °C, 2 °C/min ramp to 150 °C, 3 °C/min ramp to 280 °C, hold for 15 minutes. For the MS, a heated transfer line (300 °C) was positioned in an electron impact (EI) ionization source operating at 70 eV. A quadrupole mass analyzer scanning the 40-550 m/z range at a rate of 2.94 scans per second. Each sample was analyzed in triplicate to assess the precision of the instrument as well as the injection technique.

For each diesel sample, the data files of the TIC were extracted as Comma Separated Values (CSV) files, along with the data files of the individual EICs for aliphatic compounds (m/z 57) and aromatic compounds (m/z 91). Once all diesel samples were analyzed, their individual data files were compiled into one set for the TIC and one set for each EIC using Microsoft Excel spreadsheet software (Redmond, WA). The Diesel.M method contains a 15 minute hold at the final temperature to serve as a cleaning step between runs and to prevent carryover. Prior to data analysis, the data points corresponding to this extended hold, from 80.51 minutes to 108.33 minutes, were removed from the files since they contained no information about the samples

themselves. Once truncated, each chromatogram, both TIC and EIC, contained 13,531 data points, all of which were used in subsequent data analysis.

3.3 Data Pre-treatment

The compiled data sets for the TICs and each EIC were taken through a series of pre-treatment steps prior to data analysis. These pre-treatments served to minimize any artifacts in subsequent data analysis procedures resulting from retention time shifts and slight differences in injection volume.

First, individual data sets were subjected to a peak matching alignment algorithm available in the literature [26]. A discussion of how the alignment algorithm functions can be found in Chapter 2. The alignment was applied in order to account for minor drifts in retention time from run to run that can be caused by routine column degradation and nominal differences in the flow rate of the carrier gas. The alignment algorithm required a target chromatogram to be selected from the data set. The target was chosen at random to eliminate any potential bias from its selection. Once chosen, the target chromatogram was inserted into the data spreadsheet, and the entire file imported into Matlab (Version 7.4.0, The MathWorks, Natick, MA). After the file was imported, the target and data columns were designated variables within the Matlab workspace and the algorithm was performed. The aligned data was extracted from Matlab into spreadsheet form in Microsoft Excel for further pre-treatment.

After alignment, the data sets were normalized to overcome for slight differences in injection volume from run to run. An area normalization procedure, as described in Chapter 2, was selected as the most practical for the diesel samples. For each diesel sample, the abundance values at each retention time were summed in Microsoft Excel to

obtain the total area under the chromatogram. These sum totals were then averaged to obtain a mean area. Then, for each diesel sample, every individual data point was divided by its respective area sum, and then multiplied by the mean area sum. The multiplication by the mean was performed only to return the abundance values to the original order of magnitude.

A final pre-treatment step, mean-centering, was performed on the aligned and normalized data specifically prior to PCA. Mean-centering is applied so that the variation described by the calculated principal components is centered about the mean as discussed in Chapter 2. The aligned and normalized data was taken in Microsoft Excel, and the mean was calculated for the abundances of all samples at each individual retention time. The respective means were then subtracted from each data point to obtain the mean-centered data.

3.4 Data Analysis

Once the data sets were pre-treated, several data analysis steps were performed to determine the precision of both the instrumental technique and the injection method. Precision was assessed through both relative standard deviations (RSD) of select peak areas and PPMC coefficients.

For RSD calculations, eight peaks across the entire retention time range were selected to represent the wide array of boiling points of components contained in a diesel sample. These peaks were identified using a mass spectral search program from the National Institute of Standards and Technology (NIST, Version 2.0d, Gaithersburg, MD). The peaks were integrated in order to determine their area, which corresponds to the concentrations of the components present. The peak areas were then imported into

Microsoft Excel and normalized to the total area under the chromatographic curve, and the individual RSD values were calculated using the mean and standard deviation for each peak. For replicate analyses, peak areas should be consistent with less than 5% relative standard variation [38].

PPMC coefficients were also used to gauge precision. In order to calculate these coefficients, the aligned and normalized data spreadsheet was imported into Statistical Analysis Software (SAS, Version 9.1, The SAS Institute, Cary, NC) and the default internal PCA function was run. This default function performs PCA on the correlation matrix of the data instead of the usual covariance matrix, and part of the output of the function is a table of PPMC coefficients. This table was exported into Microsoft Excel while the rest of the data was discarded. For smaller data sets (less than 15 samples), the PPMC coefficients were also calculated in Microsoft Excel using the CORREL function.

For the actual association and discrimination of diesels based on their chemical composition, the PPMC coefficients calculated for the precision determination were utilized. In addition to PPMC coefficients, PCA was performed on the data sets, since PPMC coefficients only allow a pairwise comparison, while PCA allows the full data set to be assessed simultaneously. The data was aligned, normalized, and mean-centered prior to PCA. The pre-treated data was then converted from spreadsheet form to a CSV form and imported into a temporary workspace on the Michigan State University High Performance Computing Center (HPCC) servers. From this workspace, Matlab was accessed on a powerful cluster of computers from which the default PCA function (using the covariance matrix) was performed on the data. Use of the HPCC was necessary due to the large CSV file size generated from several replicate samples, each containing more

than 13,000 data points. Once PCA had been performed on the data, the scores, eigenvalues, and first three eigenvectors were saved in ASCII format in the HPCC temporary workspace. Only the first three eigenvectors could be saved due to storage space complications. The first three PCs, though, typically describe 85-90% of the variance of the sample set; thus, they are sufficient to allow association and discrimination among the samples. Once saved, the PCA files were transferred back to a personal computer where they were converted into a usable spreadsheet form in Microsoft Excel. The scores values for PC1 and PC2 for each sample were then plotted using an x-y scatterplot in Microsoft Excel. For 3D scores plots, Origin Pro graphing software (OriginLab, Version 8, Northampton, MA) was used to plot the scores values for PC1, PC2, and PC3 for each sample.

3.5 Results and Discussion

3.5.1 Initial Data Set

Initially, the ten diluted diesel samples were analyzed in triplicate in order to examine the reproducibility of the analytical method. RSD values were first calculated to assess precision. For normal error distribution, a 5% error rate indicates that the measurement falls within two standard deviations from the mean. Therefore, a threshold of 5% RSD or less is typically considered acceptable for analytical precision [38]. Peak areas that fall outside of the normally accepted range indicate imprecision in either the instrument or the injection method.

Table 3.2 lists the RSD values for eight peaks across the retention time range from the triplicate analysis of the ten diesel samples. Though some RSD values fall below the normally accepted 5% error threshold, several do not. GC-MS is widely

Table 3.2 RSD Values for Eight Peaks Across the Retention Time Range for Ten Diesel Samples Analyzed in Triplicate

Retention Time (min)	Potential Peak Identity	Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	Diesel 6	Diesel 7	Diesel 8	Diesel 9	Diesel 10	Average
20.784	dodecane	7.7%	5.9%	5.7%	0.6%	6.9%	3.3%	12.7%	4.6%	22.1%	4.8%	7.4%
26.207	1,2,3,4-tetrahydro-8-methylnaphthalene	5.9%	4.4%	13.3%	6.8%	2.1%	3.3%	9.6%	3.2%	13.2%	5.5%	6.8%
27.064	tridecane	4.7%	2.9%	2.7%	2.2%	4.0%	0.7%	5.8%	2.5%	11.1%	0.4%	3.7%
31.782	2,6,10-trimethyldodecane	4.2%	15.6%	12.4%	11.9%	10.2%	6.0%	14.9%	11.7%	9.3%	8.5%	10.5%
33.251	tetradecane	3.4%	2.2%	2.4%	2.4%	6.9%	2.4%	6.8%	3.6%	3.9%	2.3%	3.6%
39.211	pentadecane	2.0%	7.9%	4.6%	2.1%	4.2%	3.5%	4.0%	4.4%	10.5%	1.4%	4.5%
44.905	hexadecane	3.3%	6.9%	2.8%	2.5%	3.9%	2.5%	12.2%	4.8%	14.4%	8.2%	6.2%
50.327	heptadecane	4.9%	5.8%	9.8%	3.5%	7.1%	2.7%	16.9%	4.9%	15.9%	4.2%	7.6%

known for its analytical precision, as its instrumental errors tend to be insignificant. Therefore, it is more likely that the error observed in the RSD values is being introduced in the manual injection process.

An alternative method to examine reproducibility is to consider PPMC coefficients among replicates. These correlations offer some measure of the similarity between two samples. For two replicate injections of the same sample, correlation coefficients should be very close to one if both the instrument and injection method are precise. Table 3.3 shows the combinations of PPMC coefficients for the replicate analyses of the ten diesels. It should be noted that the correlation coefficients range from 0.7769 to 0.9886, with an average of 0.9581 ± 0.0519. While the minimum correlation is low (0.7769) for a replicate analysis, the average is reasonably acceptable by normal convention, in which a coefficient greater than 0.8 indicates a strong correlation [34]. But upon further consideration, this mean indicates that replicate injections of the same sample are only 95.81% similar on average, when in fact a higher degree of correlation should be attainable.

The unacceptable RSD values combined with poor correlation coefficients among replicates suggest that the analytical methodology is not sufficiently precise. Because of the well known precision of GC-MS, it is feasible that variation in the method of injection is responsible for the lack of precision. Further evidence that the injection procedure was imprecise showed in a preliminary scores plot from PCA of the ten triplicate diesels. The three replicates of each diesel should have been tightly clustered; instead, considerable spread was observed in the replicate clusters (data not shown). The consistently poor precision of the data analysis results compelled a closer look at the

Table 3.3 PPMC Coefficients for Replicate Sets of Ten Diesel Samples Analyzed in Triplicate

Diesel Sample	Replicate Pair	PPMC Coefficient
Diesel 1	1 and 2	0.9815
	1 and 3	0.9748
	2 and 3	0.9808
Diesel 2	1 and 2	0.9768
	1 and 3	0.9824
	2 and 3	0.9854
Diesel 3	1 and 2	0.9540
	1 and 3	0.9585
	2 and 3	0.9877
Diesel 4	1 and 2	0.7896
	1 and 3	0.7769
	2 and 3	0.9868
Diesel 5	1 and 2	0.9805
	1 and 3	0.9747
	2 and 3	0.9845
Diesel 6	1 and 2	0.9673
	1 and 3	0.9867
	2 and 3	0.9664
Diesel 7	1 and 2	0.9326
	1 and 3	0.9466
	2 and 3	0.9688
Diesel 8	1 and 2	0.9785
	1 and 3	0.9886
	2 and 3	0.9881
Diesel 9	1 and 2	0.8903
	1 and 3	0.9465
	2 and 3	0.9650
Diesel 10	1 and 2	0.9761
	1 and 3	0.9797
	2 and 3	0.9876
Average		0.9581
Standard Deviation		0.0519

chromatograms of the replicate samples themselves. Figure 3.1 depicts two sections (9-10 minutes and 50-51 minutes) of three overlaid chromatograms, all of which are replicate injections of Diesel 9. The chromatograms have been aligned and normalized. In the 9-10 minute range of the chromatogram (Figure 3.1a), the components in the second replicate are most abundant, while those in the first replicate are the least abundant. In the 50-51 minute range (Figure 3.1b), however, the opposite trend is observed. This change in the composition distribution among replicates is surprising, since component levels should remain constant throughout the entire range of the chromatogram. It is possible that, as seen with the high RSD values and low PPMC coefficients, an error in the manual injection method is causing this undesirable change in composition distribution. Hence, further investigation of the injection method was warranted.

Because the components found in diesels cover a very broad range of boiling points (approximately 70-400 °C), their vaporization differs in the injection port. In a normal injection technique, one μL of sample is drawn up into the syringe, which is placed into the inlet, and the sample immediately injected. This rapid injection does not allow the syringe needle to be sufficiently heated to the temperature of the inlet, which causes the less volatile components to be insufficiently vaporized. For these reasons, using the normal injection method for diesel samples introduces variability in the distribution of the compounds present by preferentially loading the column based on volatility. For example, the more volatile components in the diesel may be completely vaporized and passed onto the column while the less volatile components are only partially vaporized. The vaporization of all components is linked to both the current

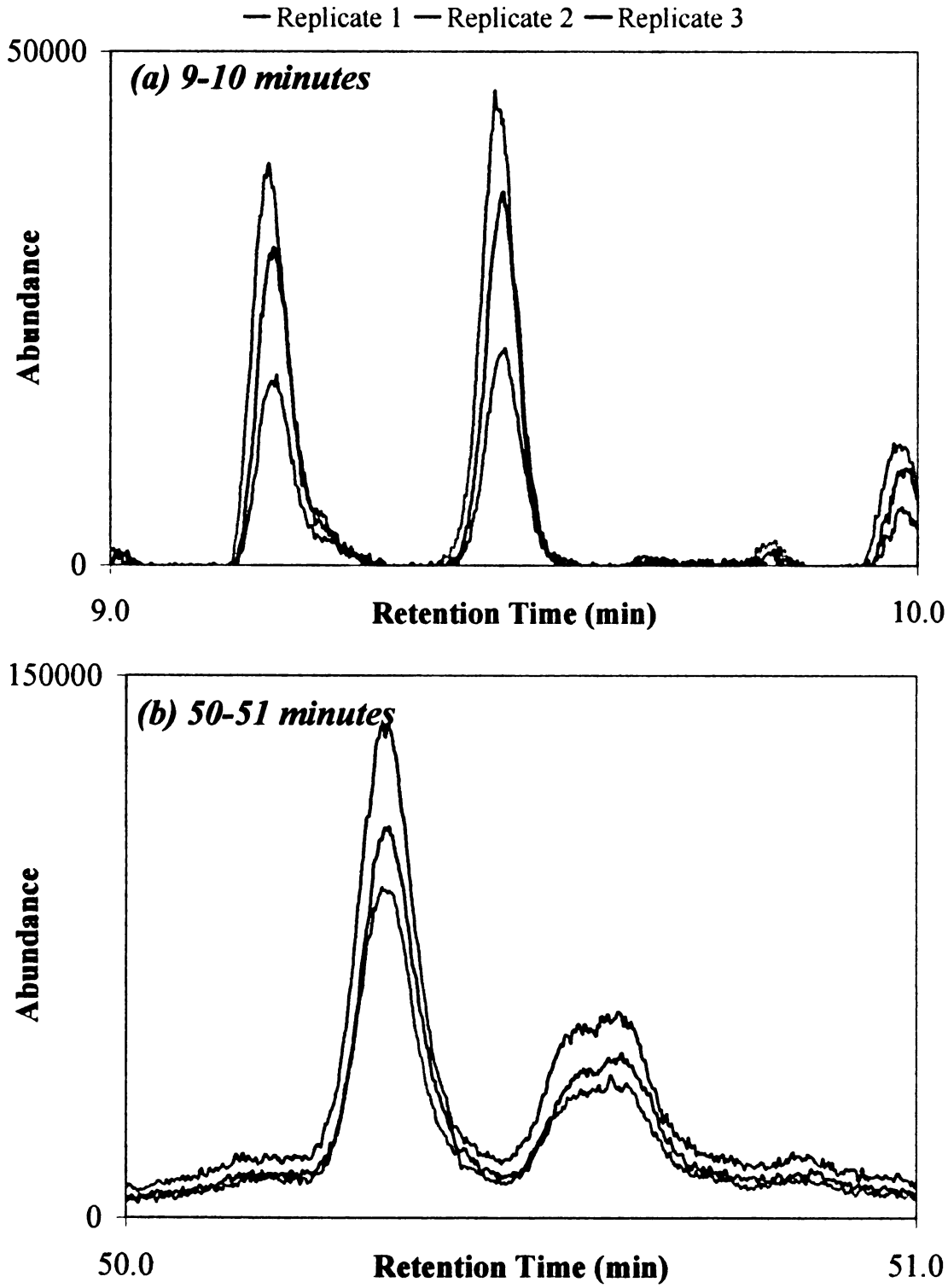

Figure 3.1 Distribution of Select Peak Areas Among Replicate Injections of Diesel 9

temperature of the injection port and the time the needle spends in the port, so that the loading preference varies with each injection as demonstrated in Figure 3.1. To overcome the volatility bias, the injection procedure was amended to draw one μL of air first, then one μL of sample, followed by another μL of air. These surrounding air pockets protect the plug of sample from the heat of the injection port until it is actually injected. The injection procedure was also changed to include a two second delay after the insertion of the needle in the inlet prior to actual injection. This timed injection allows the needle of the syringe to come to temperature without beginning to vaporize any of the sample, thus ensuring reproducible vaporization.

3.5.2 Data Set using Timed Injection

After it was determined that the original method of injection resulted in unacceptable precision in the first data set, five of the diesels were re-analyzed in triplicate using the timed injection method described above. The data was pre-treated and analyzed in the same manner as before in order to investigate the precision of the modified injection method.

The RSD values for the data from the timed injection method are listed in Table 3.4. For the same eight peaks that were examined previously, the RSD values were improved for the timed injection compared to those from the previous injection procedure. Only the RSD value for the 2,6,10-trimethyldecane peak at 31.782 minutes exceeded the 5% error threshold in all five diesels, whereas for the previous injection procedure, five of the eight peaks had unacceptable RSD values.

In addition to RSD values, PPMC coefficients were also calculated. Table 3.5 lists the correlations among replicates for the five diesels. The range of correlation

Table 3.4 RSD Values for Eight Peaks Across the Retention Time Range for Ten Diesel Samples Analyzed in Triplicate Using a Timed Injection Method

Retention Time (min)	Potential Peak Identity	Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	Average
20.784	dodecane	7.2%	8.8%	1.4%	5.2%	2.5%	5.0%
26.207	1,2,3,4-tetrahydro-8-methylnaphthalene	4.4%	5.8%	2.7%	5.3%	1.3%	3.9%
27.064	tridecane	4.3%	3.8%	3.5%	4.6%	2.3%	3.7%
31.782	2,6,10-trimethyldodecane	5.9%	9.0%	7.9%	5.6%	10.7%	7.8%
33.251	tetradecane	4.8%	5.7%	3.2%	2.4%	2.0%	3.6%
39.211	pentadecane	5.7%	1.7%	3.8%	3.2%	5.2%	3.9%
44.905	hexadecane	2.5%	1.2%	1.8%	3.2%	3.3%	2.4%
50.327	heptadecane	1.5%	2.8%	2.1%	10.4%	1.9%	3.7%

Table 3.5 PPMC Coefficients for Replicate Sets of Five Diesel Samples Analyzed in Triplicate Using a Timed Injection Method

Diesel Sample	Replicate Pair	PPMC Coefficients
Diesel 1	1 and 2	0.9884
	1 and 3	0.9870
	2 and 3	0.9878
Diesel 2	1 and 2	0.9898
	1 and 3	0.9852
	2 and 3	0.9831
Diesel 3	1 and 2	0.9870
	1 and 3	0.9659
	2 and 3	0.9599
Diesel 4	1 and 2	0.9821
	1 and 3	0.9700
	2 and 3	0.9445
Diesel 5	1 and 2	0.9850
	1 and 3	0.9721
	2 and 3	0.9846
Average		0.9782
Standard Deviation		0.0131

values among replicates, 0.9445 to 0.9898, is narrower compared to that observed in the data collected using the previous injection procedure. The average correlation value, 0.9782 ± 0.0131, indicates that the timed injection generally provides improved precision throughout replicate analysis. However, an average correlation coefficient of 0.9782 is still lower than would be expected among replicates. Although the timed injection did improve the precision of replicates, any manual injection carries the opportunity for analyst error.

3.5.3 Improving Abundance Levels of TIC and EICs

Once the precision of the injection method was established, further data analysis was performed in an effort to begin associating and discriminating the diesels based on their chemical compositions. However, through the course of this data analysis, it became obvious that the level of association and discrimination demonstrated in the PPMC coefficients and PCA results was being limited by the relatively low abundances of the chromatograms. The TICs, though low in comparison to abundances achieved through standard crime lab protocols ($\sim 10^6$-10^7) [39], were at least sufficient for analysis ($\sim 10^4$-10^5), but the real limitation occurred in the data analysis of the EICs. Because ions of a single m/z value were extracted from an already low TIC, it became difficult to differentiate peaks in the EIC from the noise level in the background. When abundances are significantly high, the variation in the baseline is insignificant, but at these low levels, any variation can create artifacts in the subsequent data analysis. In order to achieve meaningful results from the PPMC and PCA, especially from the EICs, as well as potentially improving further upon the precision of the technique, adequate abundance levels must be reached.

In order to improve the abundance levels in the chromatograms, two steps were taken. First, the dilution factor was decreased from 200:1 to 50:1 to prepare the diesel samples for GC-MS analysis. This more concentrated sample yielded TICs approximately five times more abundant than the previous 200:1 dilution. These increased abundances in the TIC allowed for more abundant EICs, though some amount of variation was still discernible in the baseline. Therefore, the second step to improve abundances was taken specifically for the EICs. The particular EICs were chosen in order to represent compound classes that are characteristic of petroleum distillates. It was determined that instead of using only a single m/z value from each compound class, multiple values from each characteristic class could be used to improve the signal-to-noise ratio for the extracted ions. The many individual ions from each class were summed to create extracted ion profiles (EIPs) for the specific compound classes. The following ions were summed to create the EIPs for their respective classes: alkane – 57 + 71 + 85 + 99; aromatic – 91 + 105 + 119 + 133; indane – 117 + 131 + 145 + 159; olefin-cycloparaffin (OCP) – 55 + 69 + 83 + 97; and polynuclear aromatic (PNA) – 128 + 142 + 156.

The EIPs offer a significant amount of additional information in comparison to a single EIC. Table 3.6 illustrates this fact by showing PPMC coefficients between single extracted ions from the same compound class and their summed EIPs for the alkane, aromatic, and indane profiles. The correlations among the individual alkane ions, as well as the correlations among the individual ions and the summed EIP, are all relatively high, which indicates that few differences exist between them and additional information is not obtained using the alkane EIP. On the other hand, the correlations for the individual

Table 3.6 PPMC Coefficients for Individual m/z Values and Their Summed EIPs for the Alkane, Aromatic, and Indane Profiles

Alkane Profile m/z Values					
	57	**71**	**85**	**99**	**EIP**
57	1.0000	0.9917	0.9876	0.9689	0.9971
71		1.0000	0.9897	0.9758	0.9972
85			1.0000	0.9794	0.9949
99				1.0000	0.9797
EIP					1.0000
Aromatic Profile m/z Values					
	91	**105**	**119**	**131**	**EIP**
91	1.0000	0.4333	0.2943	0.2558	0.7288
105		1.0000	0.2255	0.1249	0.8040
119			1.0000	0.2875	0.6470
131				1.0000	0.4171
EIP					1.0000
Indane Profile m/z Values					
	117	**131**	**145**	**EIP**	
117	1.0000	0.3990	0.2892	0.7160	
131		1.0000	0.2846	0.7599	
145			1.0000	0.7429	
EIP				1.0000	

aromatic ions and the summed EIP are very low, which suggests that the EIP contains more information than the single ions themselves. The same trend is observed for the individual indane ions and the corresponding EIP. These differences confirm that additional information concerning chemical composition is garnered from the EIP in comparison to a single EIC. These two final improvements to the method resulted in a sufficiently optimized analytical methodology and data analysis procedure.

3.5.4 Final Neat Data Set

The modifications made to the experimental and data analysis methods throughout the course of the preliminary trials were taken into account when a final neat diesel data set was analyzed. By applying the improved method, any random variations or artifacts in the results of the PPMC calculations or the PCA would be negligible. The final neat data set consisted of all ten diesels, previously described in Table 3.1, re-analyzed in triplicate. The data was compiled for the TICs, as well as the EIPs for the five characteristic compound classes (alkanes, aromatics, indanes, OCPs, and PNAs). For the TICs, RSD values were calculated of the same eight peaks as before. For the TIC and each EIP, PPMC coefficients were calculated and PCA was performed.

3.5.4.1 RSD Values

Table 3.7 shows the RSD values for the ten diesels analyzed in triplicate. As previously, RSD values for all eight peaks except the 2,6,10-trimethyldecane peak at 31.782, were lower than 5%. In fact, the RSD values for the less dilute samples were, on the whole, even lower than before. It is possible that the shape and size of the 2,6,10-trimethyldecane peak is more variable than the other peaks investigated because it is a small, shouldered peak, which would explain RSD values greater than 5%.

Table 3.7 RSD Values for Eight Peaks Across the Retention Time Range for Final Neat Diesel Data Set Analyzed in Triplicate Using a Timed Injection Method

Retention Time (min)	Potential Peak Identity	Diesel 1	Diesel 2	Diesel 3	Diesel 4	Diesel 5	Diesel 6	Diesel 7	Diesel 8	Diesel 9	Diesel 10	Average
20.784	dodecane	2.6%	3.7%	1.2%	2.8%	5.2%	1.6%	4.2%	3.7%	4.7%	7.2%	3.7%
26.207	1,2,3,4-tetrahydro-8-methylnaphthalene	1.6%	0.6%	1.6%	3.2%	6.1%	2.6%	2.0%	2.2%	1.5%	3.3%	2.5%
27.064	tridecane	3.3%	1.7%	0.7%	2.1%	0.4%	0.5%	1.7%	0.5%	0.7%	0.4%	1.2%
31.782	2,6,10-trimethyldodecane	20.0%	8.5%	1.6%	5.8%	1.7%	0.7%	11.8%	2.3%	4.6%	2.7%	6.0%
33.251	tetradecane	2.1%	0.7%	0.6%	2.4%	2.1%	1.0%	2.5%	1.4%	0.3%	1.1%	1.4%
39.211	pentadecane	1.5%	0.8%	0.8%	1.6%	2.3%	0.7%	2.3%	1.5%	4.2%	1.0%	1.7%
44.905	hexadecane	1.3%	1.2%	0.4%	3.3%	2.2%	0.6%	4.1%	0.3%	2.1%	3.5%	1.9%
50.327	heptadecane	5.6%	0.5%	1.2%	8.2%	5.5%	0.2%	7.6%	1.8%	3.5%	2.5%	3.7%

3.5.4.2 PPMC Coefficients

The PPMC coefficients for triplicate analysis of the ten diesel samples were utilized to determine the range of correlations that corresponds to diesels of known similar origin. Correlation coefficients between two samples of different origin must fall outside this range in order to be considered statistically distinguishable from the replicates. Table 3.8 lists average correlation coefficients and observed ranges among replicates for the TICs and each of the EIPs. It should be noted that correlations are highest among replicates in the TICs (0.9895 ± 0.0072), which may suggest that its potential for discrimination is higher than that of the individual EIPs. The average correlation coefficient for the TICs is higher than the previous correlation coefficient for the TICs (0.9782 ± 0.0131), which indicates that the amendments to the injection method and the dilution factor improved precision. The average correlation coefficients for the EIPs are lower than that of the TIC, which could be caused by a number of factors. It is possible that the abundance levels are still problematic though they have improved. From later data analysis, it became clear that the lower correlations for the EIPs are, however, more likely due to errors in the alignment algorithm, as discussed in the next section.

The average and standard deviation of correlation coefficients among replicates serves as a benchmark in the interpretation of PPMC coefficients for samples that are not of similar origin. Using these values, a 90% confidence interval (CI) can be calculated for the means of the PPMC coefficients for replicate samples as well as for sample pairs of different origin in order to assess statistical similarities among the diesels [27]. A confidence level of 90% was selected instead of the more conventional 95% due to the small sample size. If the 90% CI calculated for the PPMC coefficients for different

Table 3.8 PPMC Coefficients for TIC and EIPs for Replicate Sets of Ten Diesel Samples (Final Data Set)

Data Set	Average	Standard Deviation	Minimum	Maxium
TIC	0.9895	0.0072	0.9649	0.9963
Alkane	0.9824	0.0146	0.9299	0.9945
Aromatic	0.9791	0.0115	0.9376	0.9922
Indane	0.9690	0.0171	0.9157	0.9881
OCP	0.9631	0.0142	0.9271	0.9778
PNA	0.9513	0.0389	0.8163	0.9884

diesels overlaps the CI for the replicate samples, then those samples are considered the same statistically at a 90%confidence level. If the CI does not overlap that of the replicates, then the samples are considered statistically different. The CI for the PPMC coefficients is more useful than the empirical range of correlation coefficients for all replicate measurements. The minimum correlation coefficient calculated between two replicates for the TIC, for example, is 0.9649, which is well outside the defined confidence interval (0.9800-0.9989). With the opportunity for occasional disparity in the manual injection, outliers, though rare, have to be anticipated.

Using the confidence intervals for each data set, the PPMC coefficients for samples of known different origin could be assessed for any potential association and discrimination capabilities. The complete PPMC tables for each data set are shown in Appendix B. Again, for some sample pairs, such as Diesels 6 and 8, the correlation for the TICs (0.9875-0.9944) is similar statistically to that of the replicates (0.9800-0.9989), which indicates that those two samples are not statistically different. However, Diesels 2 and 3 (0.8859-0.8976) are less correlated than the replicate TIC samples, and those are statistically different. It should be noted that the range of correlation coefficients observed are typically wider for the EIPs. For example, the minimum correlation among the TICs is 0.8668. While the minimum for the alkane EIP is similar (0.8727), the minima for the other EIPs are considerably lower (aromatic – 0.7440, indane – 0.7594, OCP – 0.8380, PNA – 0.6675). This wide range of correlation coefficients may indicate that these compound classes are more discriminatory than the TIC as a whole. However, the average correlation coefficients for replicates based on these EIPs are much lower than that of the TIC, which limits the statistical discrimination capabilities to those

samples that fall below that decreased range. These two contradicting properties place some amount of question on the validity of the application of PPMC coefficients to EIPs. If still low abundance levels or misalignments are indeed the sources of error for the EIPs, then it is possible that they can be corrected and more reliable information can be gained from the EIPs. Currently, however, any data interpretation is limited to the lower average correlation thresholds established by the replicates.

3.5.4.3 PCA

PCA was also performed on the final data set using the TIC and each EIP. The scores plots for the TIC are shown in Figure 3.2. In Figure 3.2a, PC1 is plotted against PC2, where PC1 accounts for 35% of the variance, and PC2 31%. This plot affords a moderate amount of discrimination among the samples while still maintaining tight clustering of replicate samples. Diesels 1 and 2 are separated from the rest of the large cluster of samples in PC2, as PC1 appears to only distribute the samples while exhibiting very little discrimination. The separation afforded in PC2 indicates that explicit differences in chemical composition contribute to the variance described by that principal component, whereas the even distribution in PC1 indicates that a uniform range of variables contributes to its described variance. However, even within PC1, some amount of sample discrimination can be determined. For example, although Diesels 5 and 6 fall within that large group, they are significantly different in the first principal component. Other samples, however, such as Diesels 9 and 10, are very close to one another within that large grouping, so it can be reasonably concluded that these samples are not sufficiently distinguishable. With the addition of PC3 in the three-dimensional (3D) plot, further discrimination is observed. The third principal components accounts for 16% of

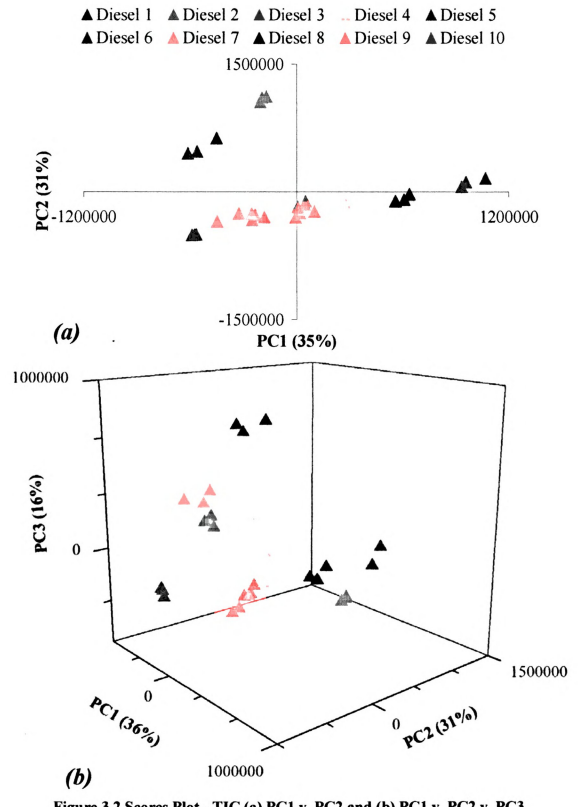

Figure 3.2 Scores Plot - TIC (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

the variance, for a total of 82% described by all 3 PCs. Diesels 1 and 2 are still separated, but the addition of PC3 allows for differentiation within the larger cluster observed in the two-dimensional (2D) scores plot. Diesels 5, 6, and 8 are moderately separated in PC3. On the other hand, Diesels 3 and 7 remain closely associated with one another, as do Diesels 4, 9, and 10. The diesels in these two clusters are not distinguishable from one another, and thus are considered to be very similar in their TIC content.

Additional information about how the individual diesel samples cluster can be garnered from the scores plots of the five different EIPs. The scores plots for the alkanes are shown in Figure 3.3. The 2D plot, in which PCs 1 and 2 describe 45% and 12% of the variance respectively, does not offer any further discrimination than the TIC. While Diesels 1 and 2 are still reasonably separated in both PC1 and PC2, the rest of the samples are scattered amongst themselves. Even the replicates are less tightly clustered, as PC2 tends to spread them. For example, the replicates of Diesels 4 and 7 are so widely spread, it would difficult to even associate them with one another. When PC3 is also included for the 3D plot, an additional 9% of the variance is described, for a total of 66%. PC3 does nothing to further associate or discriminate samples. In fact, it causes additional spread in the replicate diesels. Similar trends are observed in both the 2D and 3D scores plots for the indane and PNA profiles, which are shown in Figures 3.4 and 3.5. Diesels 1 and 2 are still somewhat separated from the main cluster, but the spread in the replicates is even worse (again, likely due to misalignments in the EIPs). It is possible that the diesel samples do not vary greatly in their alkane, indane, or PNA content, which would explain the lack of discrimination in the scores plots. A brief visual comparison of overlaid chromatograms for different diesels for each profile indicated that some amount

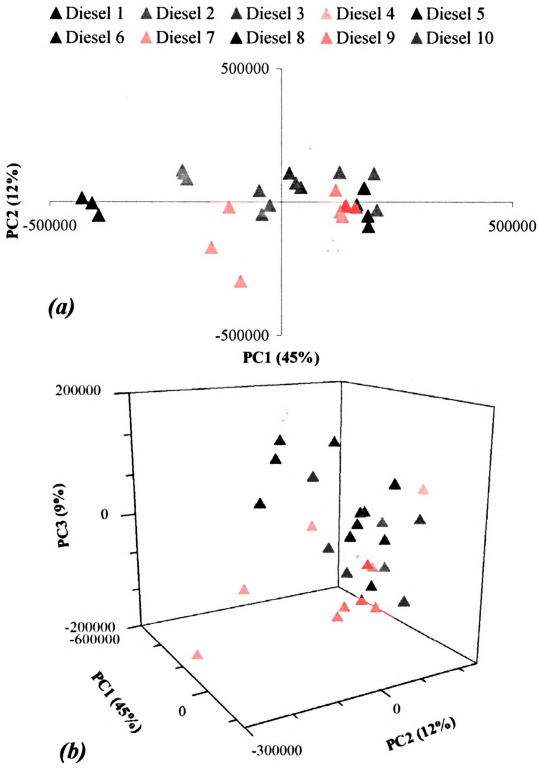

Figure 3.3 Scores Plot - Alkane EIP (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

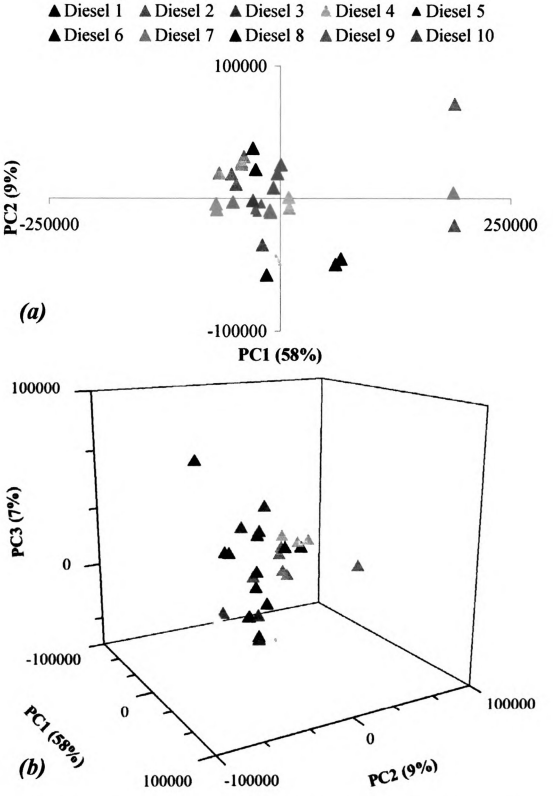

Figure 3.4 Scores Plot - Indane EIP (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

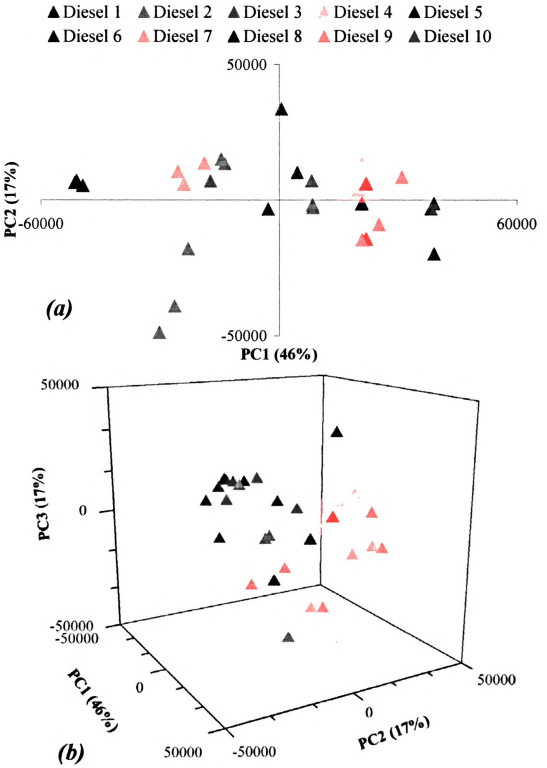

Figure 3.5 Scores Plot - PNA EIP (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

of variation is noticeable, while some areas are very similar. It is likely that the differences are not significant enough to be isolated by PCA, which would imply that these compound classes are not useful for determining association and discrimination among the diesels.

The other two compound classes, however, do provide discrimination of the diesels in their scores plots. The scores plots for the aromatic profiles, Figure 3.6, show tight clustering for replicates. In the 2D plot, Diesels 1 and 2 are still isolated from the main cluster, but in this case, that main cluster is not spread about the first principal component as it was in the TIC. Instead, the eight other diesels are very tightly clustered, which suggests that they are all very similar in their aromatic content. The 3D plot demonstrates the same trend, though PC3 spreads the tightly clustered eight diesels, as Diesels 5 and 7 begin to be separated from the larger group. The differentiation in PC3 is difficult to discern, however, it only describes a small amount of the total variance (3%) in comparison to PCs 1 and 2, 75% and 8% respectively. The scores plots from the OCP profile, shown in Figure 3.7, afford a considerable amount of discrimination than the other profiles. Replicates are still closely associated in the 2D plot, with the exception of Diesels 2 and 8, which are spread in comparison to the other replicates. This spread could be caused by a number of different factors, though the most likely source is possible misalignment. Individual diesel samples, most notably Diesels 1 and 2, are beginning to be isolated in the 2D plot as well, though it should be noted that their separation is only due to 48% of the total variance of the data. The 3D plot, which includes an additional 10% of the variance, exhibits similar traits to the 2D plot. Replicate spread worsens in PC3, though on a minor level, some diesels are more

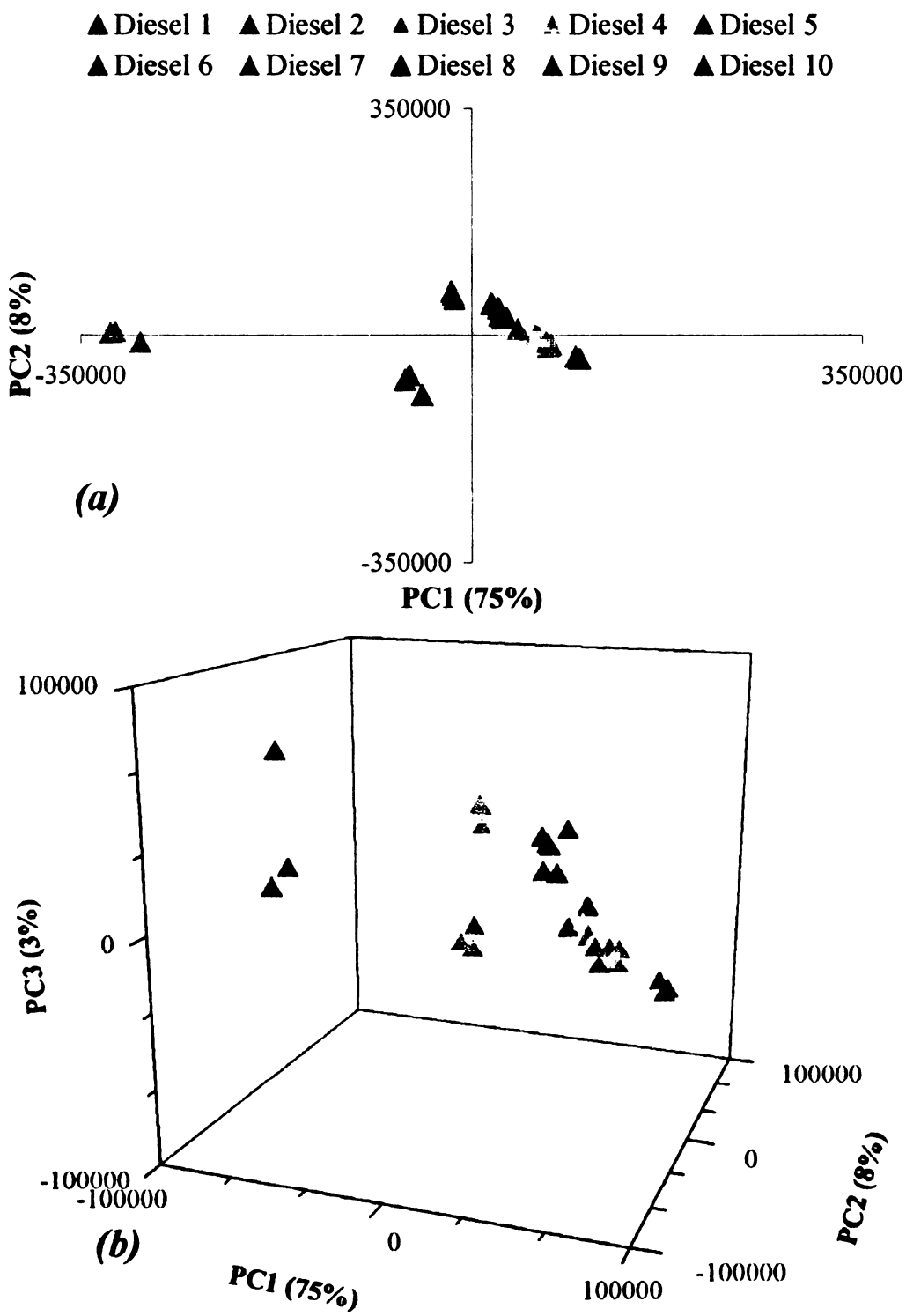

Figure 3.6 Scores Plot - Aromatic EIP (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

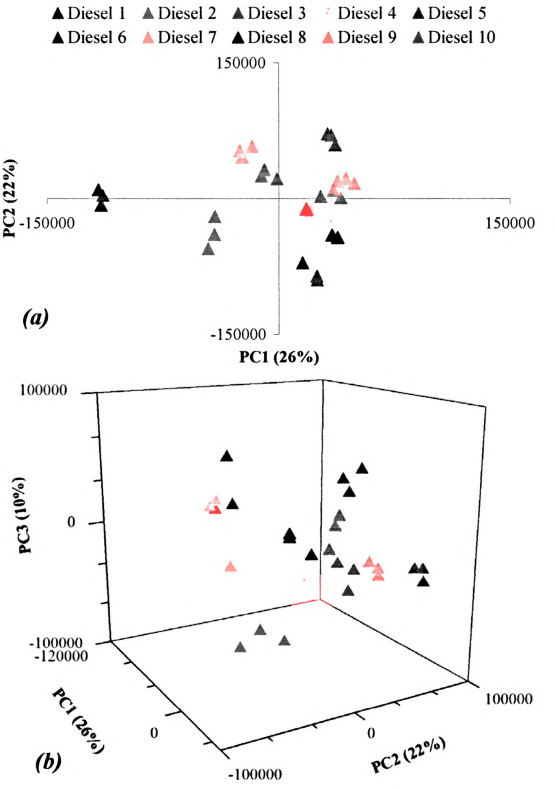

Figure 3.7 Scores Plot - OCP EIP (a) PC1 v. PC2 and (b) PC1 v. PC2 v. PC3

separated. For example, in the 2D plot, Diesels 4 and 8 are closely associated, but in the 3D plot, they are more separated in PC3. Based on these results, the aromatic and OCP profiles are more useful in associating and discriminating diesels than the alkane, indane, and PNA profiles.

In addition to the scores plots, PCA also provides information about which components in the samples contributed most to the determination of each principal component. This eigenvector, which can be displayed in a loadings plot, determines how the score of a sample is calculated. The loadings plots for the first and second principal components of the TICs are shown in Figure 3.8. It is clear that, while the alkane components dominate the loadings for the first PC (Figure 3.8a), a mixture of compounds from other characteristic classes is responsible for separation along the second PC (Figure 3.8b). The fact that the alkanes dominate PC1 does not necessarily indicate that they are the primary source of variation among the diesels. In fact, the diesels are not clearly separated along PC1 in the TIC as shown in Figure 3.2; they are relatively evenly distributed by their differences in alkane content. The lack of sufficient clustering of the diesels in the scores plot of the alkane profiles also indicates that the alkanes alone are not adequate for associating and discriminating the samples. The presence of components other than alkanes at lower levels in PC1 and at higher levels throughout PC2 implies that some combination of aliphatics and non-aliphatics is responsible for the discrimination among the diesels demonstrated in the scores plots for the TIC (Figure 3.2).

The loadings plot is not only useful for determining the components contributing the most to the eigenvectors, it can also highlight any anomalies caused by the analytical

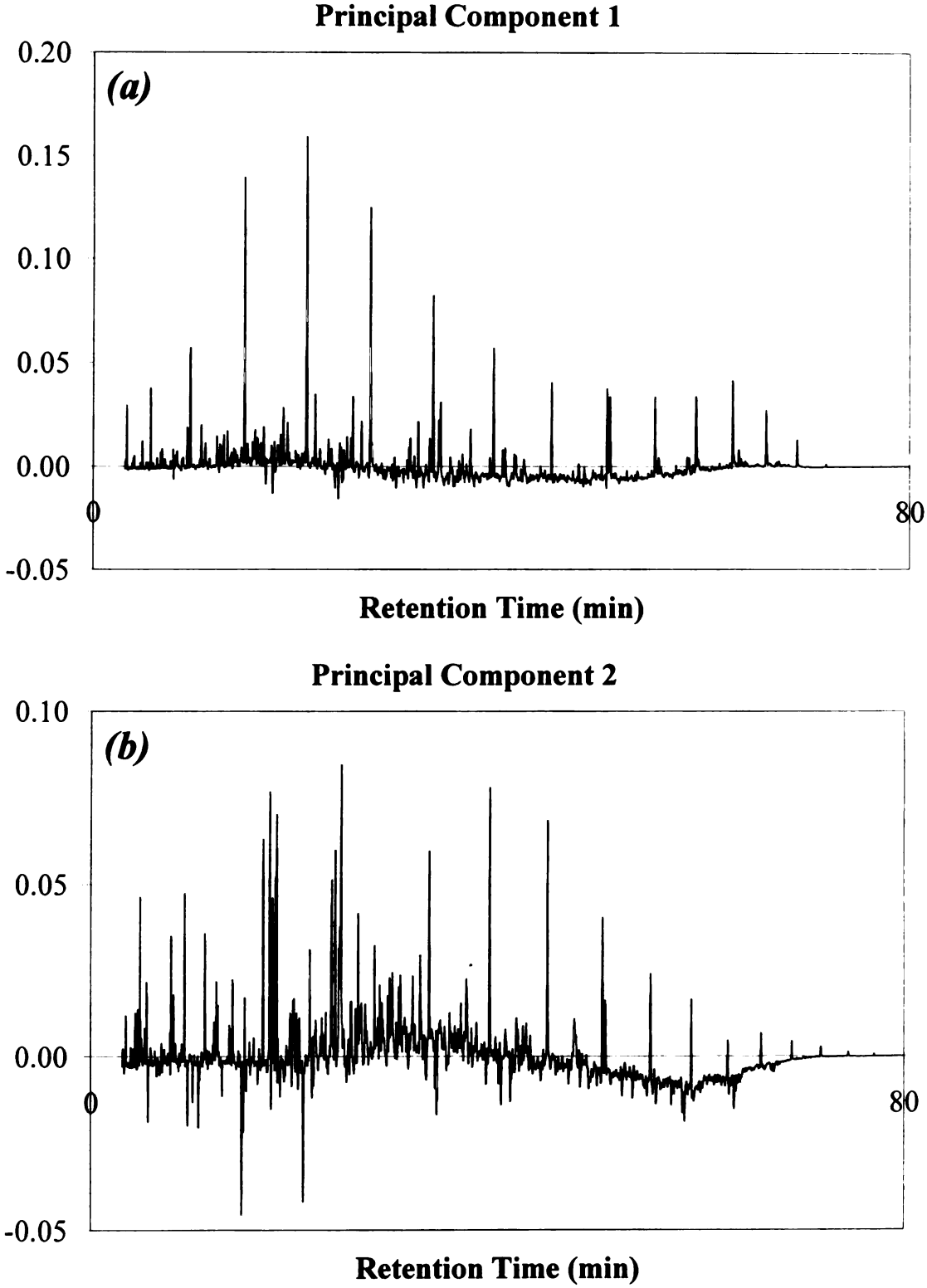

Figure 3.8 Loadings Plots of First Two Eigenvectors from PCA of the TICs of Ten Diesels Analyzed in Triplicate

technique or the data pre-treatment steps that can potentially contribute to the sources of variation observed in scores plots. For example, in the loadings plot for the first two PCs of the alkane EIP, shown in Figure 3.9, several derivative-shaped curves are noticeable. In fact, these derivative-shaped peaks dominate the second eigenvector (Figure 3.9b). Not normally observed in loadings plots, these peaks are indicative of an artifact in the samples. Because these peaks are not observed in the loadings plots for the TICs, it is possible that the artifact causing them has been introduced in the data pre-treatment steps. The most likely source of error is in the alignment procedure. Figure 3.10 overlays three replicate chromatograms of Diesel 1 around the peak with a retention time of approximately 33 minutes, which corresponds to derivative-shaped curves in the first two PCs as shown in Figure 3.9. It is obvious that this peak has been misaligned for this sample. Further inspection revealed that this peak has been misaligned throughout the alkane EIP data set, and this introduction of error in the data pre-treatment stage has propagated through to the data analysis results. The increase in range for the correlation coefficients of the replicates, as well as the spread observed among the replicates in the scores plots, can most likely be attributed to significant misalignments. It can be concluded that the alignment algorithm is by no means perfect, and misalignments must be considered when the PPMC and PCA results are being interpreted.

In the analysis of a neat diesel data set, several obstacles were encountered and overcome. A precise manual injection method was developed, and sufficient abundance was achieved for accurate PPMC coefficients and PCA results. It was then demonstrated that PPMC coefficients and PCA were sufficient for the association and discrimination of neat diesels based on chemical composition.

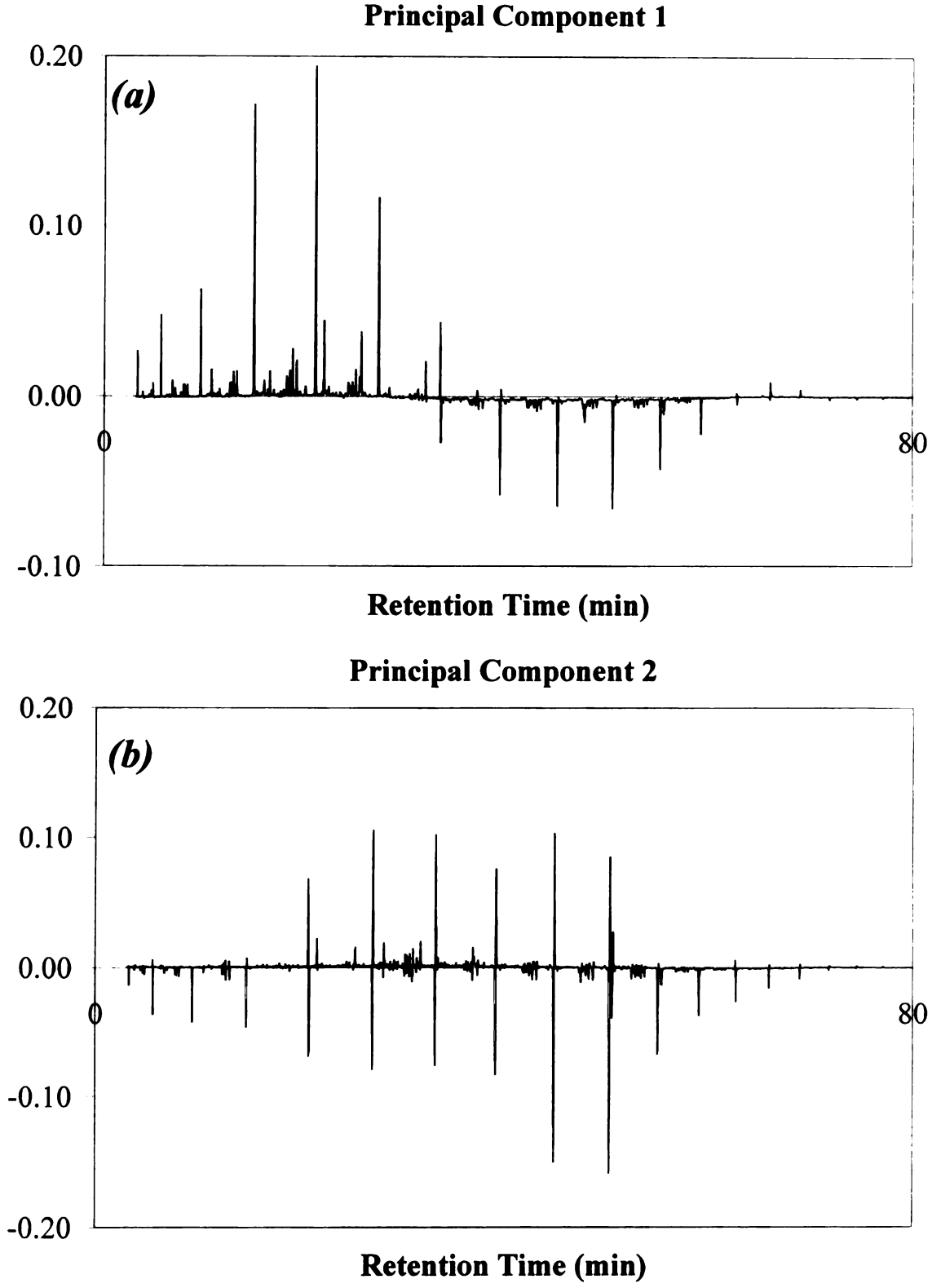

Figure 3.9 Loadings Plots of First Two Eigenvectors from PCA of the Alkane EIPs of Ten Diesels Analyzed in Triplicate

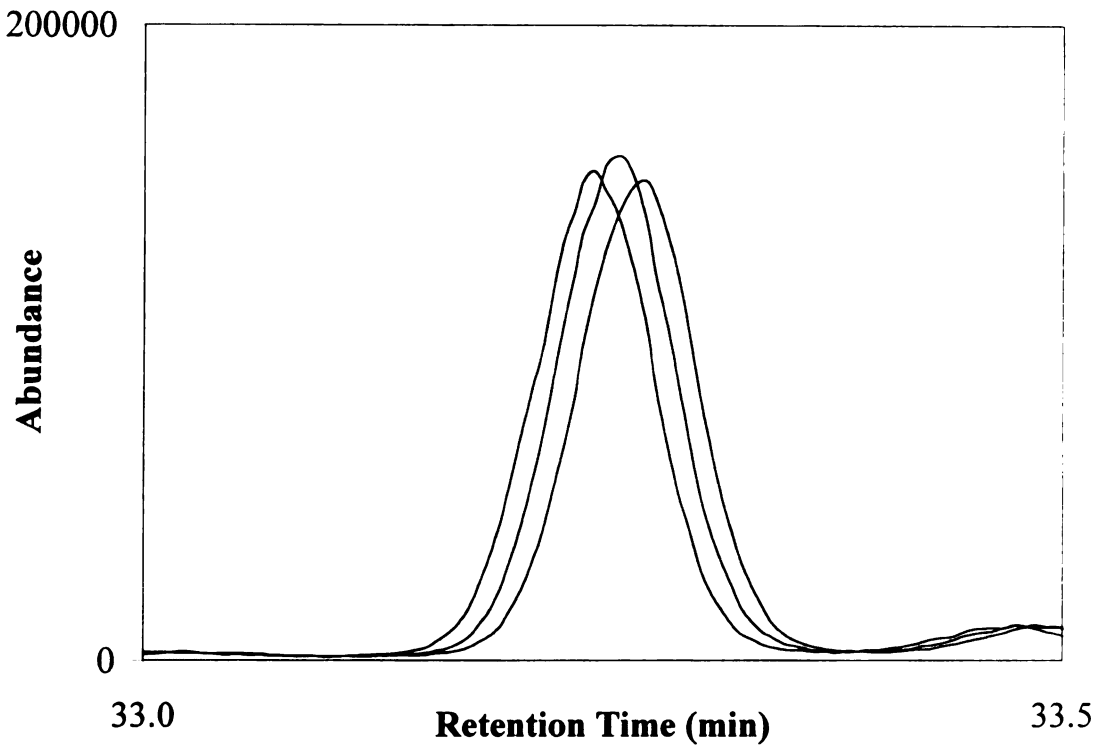

Figure 3.10 Misaligned Peak in the Alkane EIPs of Diesel 1 Replicates

Chapter 4

Association and Discrimination of Burned Diesels Extracted from Fire Debris Using PPMC Coefficients and PCA

4.1 Introduction

The substantiation of the principle that diesels can be associated and discriminated based on variation in chemical composition by chemometric procedures (PPMC coefficients and PCA) was demonstrated in Chapter 3. These procedures, however, possess the potential for applications past the association and discrimination of neat diesels alone. The next step in the research then is to investigate the associative and discriminatory potentials of these chemometric procedures for diesels that have been burned and extracted from fire debris. These conditions are more similar to those encountered in an actual arson case, and are therefore more practical in a forensic laboratory setting.

When ignitable liquids are utilized as accelerants, they are often poured throughout the structure and then ignited in order to start the fire and guarantee its spread. The ignitable liquid can be affected in many ways both during the fire as well as while the fire is being extinguished. While much of the ignitable liquid is consumed in the burning process, it can also be absorbed by the substrate on which it was poured, where it remains protected to some extent from the heat of the fire. More porous substrates, such as wood and carpet, have a greater potential for retention of ignitable liquids, and these substrates are frequently sampled in fire debris analysis.

Although the ignitable liquid can be absorbed by porous substrates and shielded from the fire, the intense heat is still capable of causing the loss of the more volatile

components present in the ignitable liquid. For these reasons, the chromatograms obtained from the GC-MS analysis of ignitable liquid residues (ILRs) extracted from fire debris are often skewed toward the less volatile components—that is, the chromatograms contain more of the less volatile components and little to none of the more volatile components. This distortion in chemical composition may lead to a misidentification of an ignitable liquid when a visual assessment of chromatographic patterns is performed. However, the application of chemometric procedures such as PPMC coefficients and PCA to associate and discriminate the burned ignitable liquids is more objective in nature, which could potentially overcome the subjectivity issues of a visual assessment. These procedures can be performed on not only the TIC, which may potentially be too skewed to be associated to its neat counterpart, but also on the EIPs of the characteristic compound classes of ignitable liquids. The classes that consist of mostly low volatile compounds may be more discriminatory than the TIC or other compound classes that are more significantly affected by the burning process.

In order to investigate the potential for associating a burned diesel extracted from fire debris to its unburned counterpart, a complete set of burning experiments was performed on a newly collected set of diesels. Since a new instrument was used for this part of the research, the precision of the instrument as well as the injection method was re-assessed with the analysis of a new set of neat diesels. These diesels were analyzed in triplicate to examine the association and discrimination observed among the new sample set. Prior to conducting the burning experiments, Diesel 21, chosen at random, was spiked onto three different matrices (cotton cloth, magazine, and carpet) and a series of spike and recovery studies were performed to examine the efficiency of the solvent

extraction procedure selected. Then, Diesel 21 was subjected to a series of burning conditions on the three different matrices. For each matrix, five analyses were performed in triplicate: unburned matrix, burned matrix, unburned then spiked (50 μL) matrix, burned then spiked matrix, and finally a spiked then burned matrix to simulate actual arson conditions. The final phase was to perform a blind association study in which two diesels that had been previously analyzed were treated as unknowns. The blind diesels were spiked separately onto each of the three matrices and then burned. The debris was extracted and analyzed in an attempt to associate the blind diesel sample to its neat counterpart. PPMC coefficients and PCA were used to associate and discriminate the diesels, both burned and unburned, based on chemical composition.

4.2 Analysis of New Set of Neat Diesels

4.2.1 Procedure

Five of the previous ten diesel samples (Table 3.1) were re-collected from various Lansing service stations during the winter. Table 4.1 lists the samples and the details of their collection. After collection, the diesels were stored as described previously in Chapter 3.

The five neat diesels were analyzed in triplicate by GC-MS, using a newly purchased instrument. The GC was the same make and model number (Agilent 6890 GC) as previous, while the MS was a newer version of the previously used MS (Agilent 5975 MSD compared to Agilent 5973). After initial analyses of the freshly collected diesel samples, it was observed that, in order to obtain chromatograms of similar abundances to before, a different dilution (10:1 in CH_2Cl_2 instead of 50:1) of the neat diesels was necessary. The higher abundance levels in the TIC are essential in order for

Table 4.1 Diesel Collection Log

Sample	Service Station	Location	Date of Collection	Color at Time of Collection
Diesel 21	Sunoco	2139 Haslett Road	01/10/08	fluorescent yellow
Diesel 22	Sunoco	3000 Dunckel Road	01/28/08	pale yellow
Diesel 23	Meijer	2055 West Grand River Avenue	01/28/08	fluorescent yellow
Diesel 24	Speedway	1659 Grand River Avenue	01/31/08	fluorescent yellow
Diesel 25	Mobil	1500 Haslett Road	01/31/08	fluorescent yellow

the peaks present in the EIPs to be sufficiently distinguished from baseline noise. The sensitivity discrepancies between the two instruments are most likely due to minor discrepancies in the mass spectrometer, such as the position of the column in the ionization source or the voltages of the accelerating lenses. It was also concluded that the previous temperature program used was too long (108.33 minutes) to be practical in a forensic laboratory setting. The temperature program employed by the National Center for Forensic Science (NCFS) and the Technical Working Group for Fire and Explosions (TWGFEX) to generate the Ignitable Liquid Reference Collection (ILRC) was used instead [40]. This temperature program (NCFS.M) was as follows: initial temperature 50 °C, hold for 3 minutes, 10 °C/min ramp to 280 °C, hold for 4 minutes. The total run time was reduced to 30 minutes. All other instrumental parameters were the same as described in Chapter 3.

Preliminary assessments of the chromatograms, both of the TIC and each EIP, indicated that the change to the temperature program did not noticeably sacrifice any chemical features. The increase to the ramp rate, however, offered a significant improvement in total analysis time which, in turn, allows for the methodology to be practical in the traditionally backlogged setting of an operating forensic laboratory. This compromise between improved analysis time and retention of discriminatory chemical features is a necessary consideration in the development of this methodology.

Once the neat diesel data were collected and analyzed, the TIC and the ions used to generate the five EIP sets were extracted into Microsoft Excel as described in Chapter 3. The shorter temperature program, however, eliminated the need for truncating the end of the chromatograms. For the diesels analyzed by the NCFS.M method, each

chromatogram consisted of a total of 4702 data points (compared to 13,000 data points previously), all of which were considered in subsequent data analysis. The data were pre-treated as described in Chapter 3. RSD values and PPMC coefficients were also calculated for the TICs in order to demonstrate the precision of the new GC-MS instrument. The TIC and EIPs were also analyzed by PPMC coefficients and PCA in order to evaluate the association and discrimination of the neat diesels based on chemical composition.

4.2.2 Results and Discussion

Initially, RSD values were calculated to demonstrate the precision of the instrument. Table 4.2 lists the average RSD values for eight peaks throughout the chromatographic range for triplicate analyses of the five diesels. For the same eight peaks as selected in Chapter 3, average RSD values were well below the accepted threshold of 5% [38]. For previous average RSD values for the timed injection, one of the eight peaks still exhibited an RSD of greater than 5%. The lack of precision for that peak has been eliminated in this data set. It should be noted that the RSD values for Diesel 21 are higher than those of the other samples, which could indicate an aberration in the timed injection procedure for one of the replicate analyses for Diesel 21. However, all the average RSD values were below 3% which indicates that the instrumental technique and the injection method are precise.

PPMC coefficients were also calculated to assess precision among replicate analyses. Table 4.3 lists the PPMC coefficients for the replicate analyses of the five diesels based on the TIC. Correlation coefficients for the replicate analyses ranged from 0.9780 to 0.9975, with an average of 0.9921 ± 0.0061. This correlation is higher than

Table 4.2 RSD Values for Eight Peaks Across the Retention Time Range for Five Diesel Samples Analyzed in Triplicate

Retention Time (min)	Potential Peak Identity	Diesel 21	Diesel 22	Diesel 23	Diesel 24	Diesel 25	Average
10.623	dodecane	5.1%	3.9%	0.5%	0.2%	1.9%	2.3%
11.648	1,2,3,4-tetrahydro-8-methylnaphthalene	5.0%	4.7%	0.8%	0.8%	0.8%	2.4%
12.075	tridecane	2.9%	0.6%	0.8%	0.3%	0.9%	1.1%
13.115	2,6,10-trimethyldodecane	7.4%	1.5%	1.1%	1.0%	1.5%	2.5%
13.426	tetradecane	5.4%	0.6%	0.9%	0.1%	0.8%	1.6%
14.693	pentadecane	3.9%	0.7%	2.8%	0.3%	2.6%	2.0%
15.886	hexadecane	4.6%	1.0%	0.4%	0.6%	2.7%	1.8%
17.018	heptadecane	7.0%	0.7%	1.8%	0.6%	0.5%	2.1%

Table 4.3 PPMC Coefficients for the TIC of Replicate Sets of Five Diesel Samples Analyzed in Triplicate

Diesel Sample	Replicate Pair	PPMC Coefficients
Diesel 21	1 and 2	0.9941
	1 and 3	0.9962
	2 and 3	0.9975
Diesel 22	1 and 2	0.9879
	1 and 3	0.9841
	2 and 3	0.9899
Diesel 23	1 and 2	0.9908
	1 and 3	0.9836
	2 and 3	0.9780
Diesel 24	1 and 2	0.9969
	1 and 3	0.9967
	2 and 3	0.9969
Diesel 25	1 and 2	0.9955
	1 and 3	0.9973
	2 and 3	0.9956
Average		0.9921
Standard Deviation		0.0061

that of a previous data set run on a different instrument (0.9895 ± 0.0072) as described in Chapter 3. This high correlation indicated that the new instrument was precise.

As discussed in Chapter 3, 90% confidence intervals (CI) for the average PPMC coefficient for replicate analyses for the TICs and EIPs were used as the threshold for the comparison of samples from different origins [27]. If a CI for a diesel pair of different origin overlaps with the CI defined by the replicates, then that pair would be considered statistically indistinguishable. On the other hand, if the CI for that pair did not overlap the CI as determined by the replicates, then the diesel pair could be considered statistically distinguishable. The average correlation coefficient and respective standard deviations are given in Table 4.4 for the TIC and each EIP set for triplicate analyses of the five diesels. It should be noted that, on the whole, a higher level of association among replicates for the EIPs is observed as compared to previous data sets (Chapter 3). This narrow range for replicates improves the discrimination capability afforded by each EIP.

Data analysis was initially performed on the neat diesel data set in order to determine the sources of variance in chemical composition among the new set of five diesels. PPMC coefficients were calculated for all diesel pairs in the TIC data set as well as each EIP compilation (alkane, aromatic, indane, OCP, and PNA). Each data set was also subjected to PCA, and scores plots were generated to assess the natural clustering of the diesels based on their inherent chemical composition.

The complete PPMC coefficient tables for each data set are shown in Appendix C. The 90% CI for the replicates for the TIC was calculated to be 0.9813 – 1.0029. When examining CIs for different diesel pairs, Diesels 21 and 23 (0.9688 – 0.9934), Diesels 21

Table 4.4 PPMC Coefficients for TIC and EIPs for Replicate Sets of Five Diesel Samples

Data Set	Average	Standard Deviation	Minimum	Maximum
TIC	0.9921	0.0061	0.9780	0.9975
Alkane EIP	0.9729	0.0384	0.8788	0.9971
Aromatic EIP	0.9813	0.0145	0.9597	0.9984
Indane EIP	0.9960	0.0019	0.9916	0.9987
OCP EIP	0.9869	0.0086	0.9682	0.9973
PNA EIP	0.9910	0.0064	0.9772	0.9985

and 24 (0.9692 – 0.9818), and Diesels 23 and 25 (0.9809 – 0.9889) exhibited overlapping ranges with the CI established by the replicates, which indicated that these three pairs were statistically similar. All other sample pairs did not exhibit CIs that overlapped with the replicates, which indicated that they are statistically different. Similar observations concerning statistical similarities between diesel pairs can be made for the EIPs as well.

PCA was also performed on the neat data set using the TIC and each EIP. Only 2D scores plots are shown for these data sets for ease of comparison. The scores plot for the TIC is shown in Figure 4.1. In this plot, PC1 accounts for 53% of the variance, while PC2 accounts for 26%. The replicates for each diesel are well clustered, though the replicate clusters for Diesels 21 and 23 exhibit minor spread in PC2. For the five diesels, 89% of the variance for the first two PCs reasonably separates all five samples. Diesel 22 is significantly positive in PC1, while Diesel 24 is negative. The other three diesels are all relatively close to zero in PC1. Diesels 22 and 24 are negative in PC2, and Diesels 23 and 25 are positive. The combination, then, of PC1 and PC2 is sufficient for separation of the replicate clusters of each diesel.

Additional information about how the individual diesels cluster can be garnered from the scores plots of the five different EIPs. Figure 4.2 shows the scores plot for the alkane EIP, in which PC1 accounts for 51% of the variance and PC2 24%. The same general clustering trend as observed in the TIC scores plot can be seen in PC1 in the alkane plot. Diesel 22 is positive, Diesel 24 is negative, and Diesels 21, 23, and 25 are close to zero. However, in PC2, most sample scores are close to zero, with the exception of one triplicate analysis of Diesel 23, which is significantly distant from its replicate cluster. As discussed previously, this separation of one replicate analysis from the others

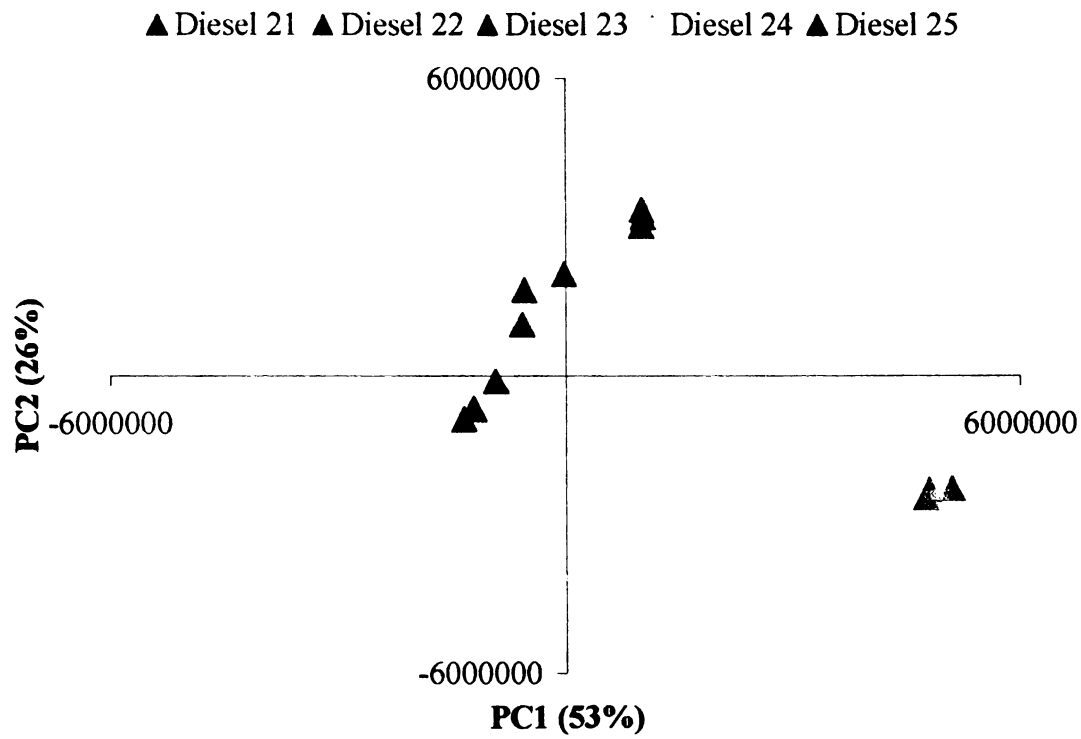

Figure 4.1 Scores Plot for the TIC of the Neat Diesels

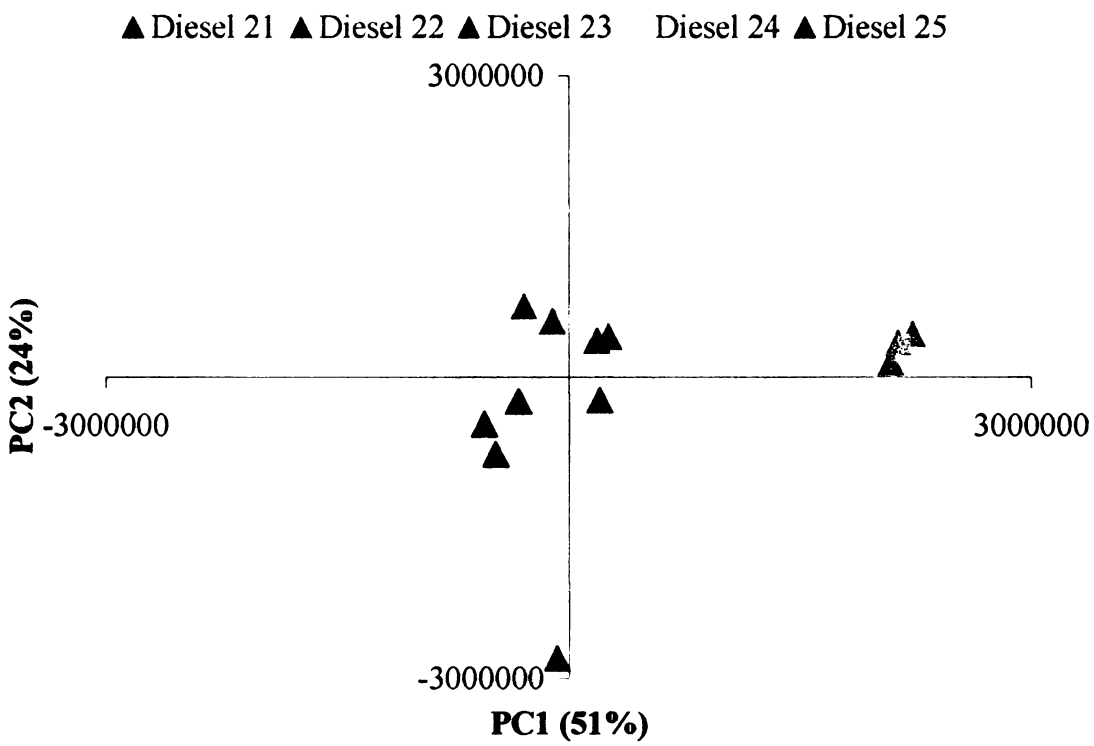

Figure 4.2 Scores Plot for the Alkane EIP of the Neat Diesels

is often due to a misalignment introduced in the data-pretreatment steps. The alkane EIP has been prone to misalignments as seen in Chapter 3, and the fact that PC2 describes 24% of the variance indicates that a considerable misalignment, or potentially more than one misalignment, has been introduced in the data pre-treatment steps for that particular replicate sample. Therefore, association and discrimination for the alkane plot can only be accurately assessed in the first principal component.

The aromatic scores plot, shown in Figure 4.3, indicates that Diesel 22 differs significantly in aromatic content than the other four diesels. In fact, the other four diesels appear to be highly similar in their aromatic content. It should be noted that the clustering of the samples in the aromatic EIP is almost completely dictated by PC1. Very little spread is observed in PC2. Because of the considerable amount of variance described by PC1 (87%) as compared to PC2 (5%), it can be assumed that PC2 does little to separate the diesels based on chemical composition. Therefore, clustering in the aromatic profile is only considered as based on PC1.

The indane scores plot, shown in Figure 4.4, shows a similar trend in PC1 to the aromatic scores plot. Diesel 22 is largely positive in PC1 (which describes 83% of the variance), while the other four diesels are each slightly negative and are not well separated from one another. However, unlike in the aromatic scores plot, PC2 (which describes 8% of the variance) contributes to the natural clustering of the samples. Diesels 23 and 25 are separated from each other in PC2, as well as from Diesels 21 and 24; however, due to minor spread in the replicate clusters in PC2, Diesels 21 and 24 cannot be reasonably separated from one another and are likely similar in indane content.

The OCP scores plot, shown in Figure 4.5, is similar in its cluster patterns to the

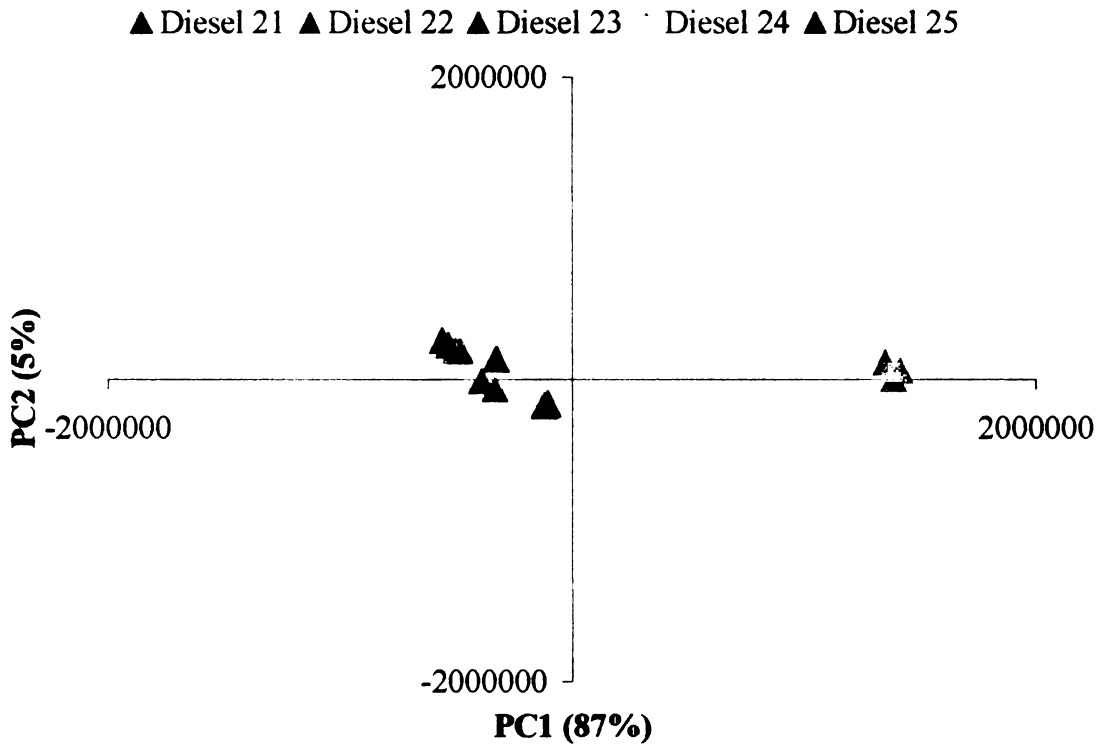

Figure 4.3 Scores Plot for the Aromatic EIP of the Neat Diesels

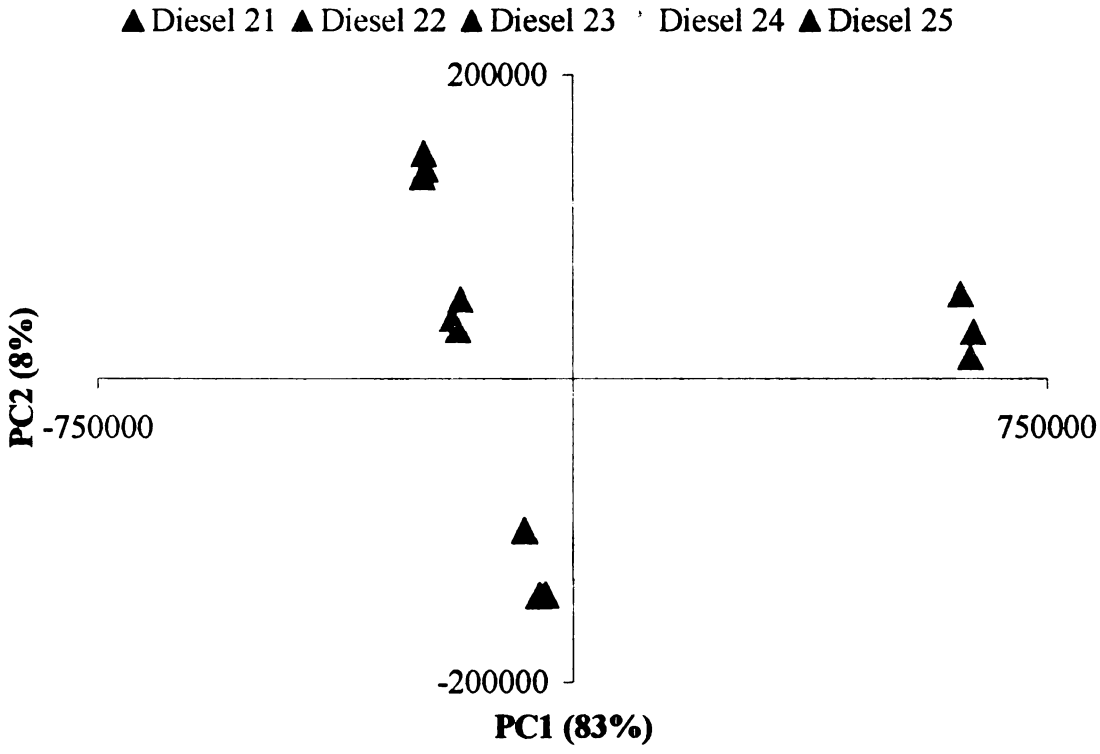

Figure 4.4 Scores Plot for the Indane EIP of the Neat Diesels

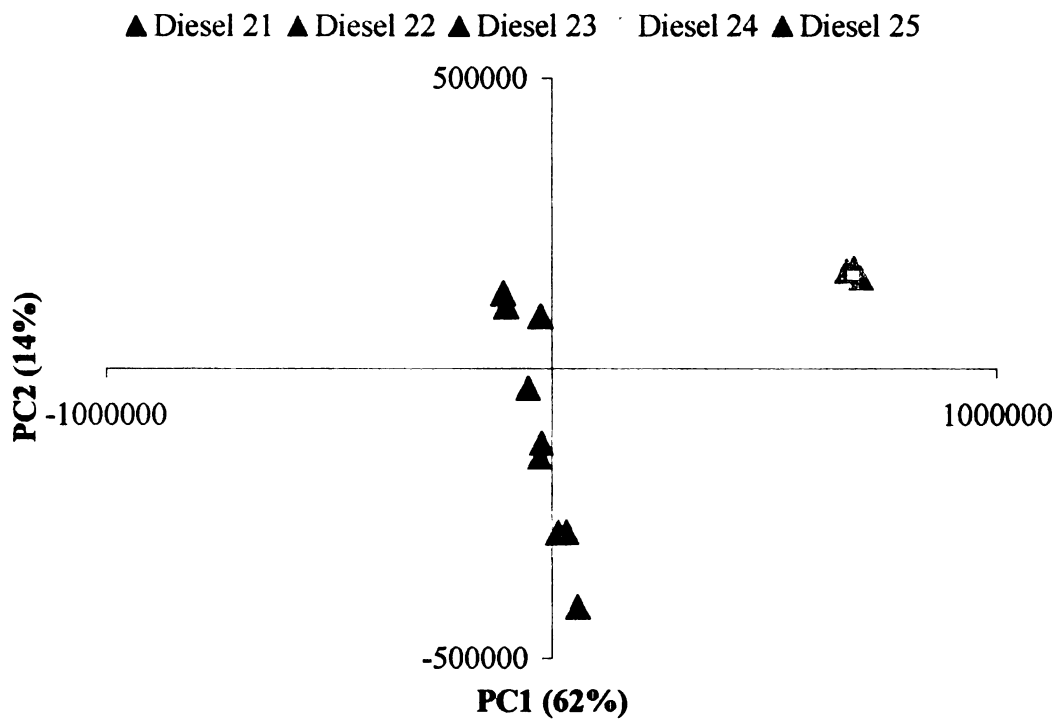

Figure 4.5 Scores Plot for the OCP EIP of the Neat Diesels

alkane scores plot (Figure 4.2). In PC1 (which describes 62% of the variance), Diesel 22 is positive, Diesel 24 is negative, and the other three diesels center around zero. However, in the alkane plot, differentiation in PC2 is potentially due to a misalignment instead of actual chemical variation. In the OCP plot, differentiation in PC2 is not characteristic of a misalignment, and it can be assumed that any discrimination is likely caused by differences in chemical composition. In PC2, Diesels 21, 23, and 25 are separated, while Diesels 22 and 24 are similar in PC2. Again, the combination of PC1 and PC2 allows for moderate separation of the five diesels in the OCP scores plot.

In the PNA scores plot, Figure 4.6 PC1 accounts for 50% of the variance, and PC2 accounts for 17%. The five diesels are somewhat separated in PC1, where Diesel 22 is negative, Diesel 21 is around zero, Diesels 24 and 25 are slightly positive, and Diesel 23 is slightly more positive. PC2 also causes separation of the samples, with Diesels 22, 23, and 25 being negative and Diesels 21 and 24 positive in PC2. When combined with the separation caused by PC1, the five diesel replicate clusters are reasonably separated from one another.

It should be observed that, with the exception of the misalignment in PC2, the clustering of the diesels in this data set is significantly improved over prior data sets, most likely due to improved precision in the manual injection method that comes with analyst experience. For example, in the final neat data set described in Chapter 3, the alkane, indane, and PNA plots were deemed less useful because they demonstrated spread in the replicates and a lack of natural clustering among the samples. In this data set (analyzed using a new instrument), however, the TICs and EIPs provide considerable association among replicates and discrimination among samples for all five diesels. This

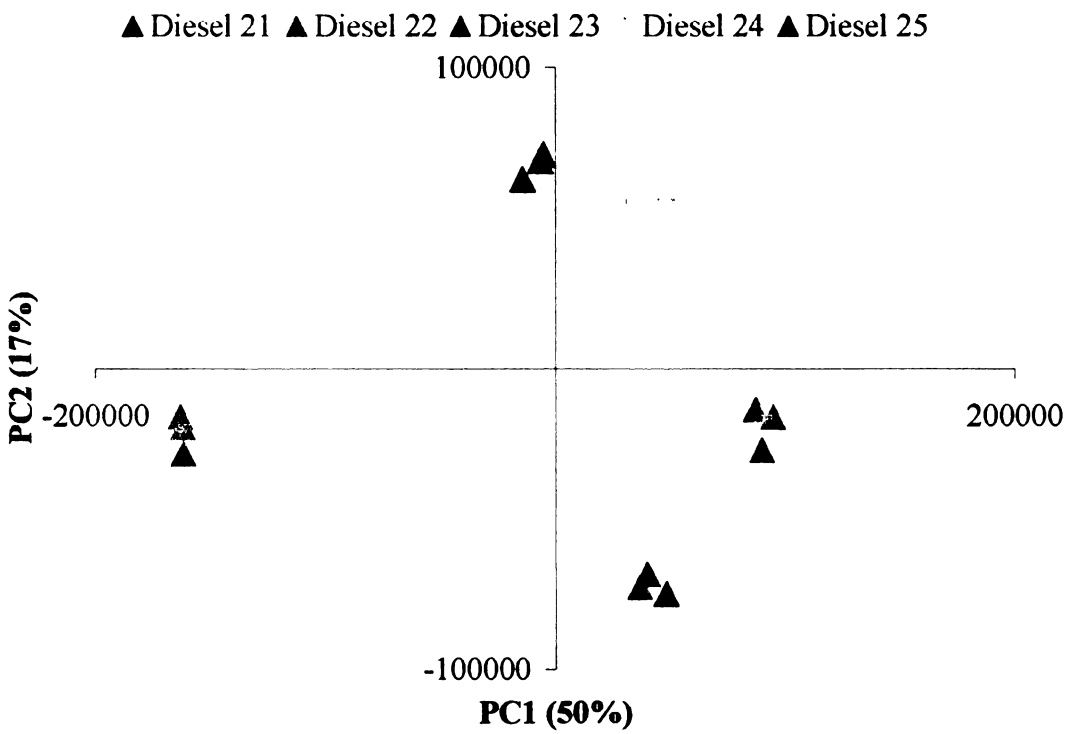

Figure 4.6 Scores Plot for the PNA EIP of the Neat Diesels

association and discrimination capability demonstrates the utility of PCA, not only for the TIC but also for characteristic EIPs, for comparing neat diesel samples.

4.3 Efficiency of Solvent Extraction Procedure

4.3.1 Procedure

After the analysis of the neat diesels, the next step was to perform the burned studies. First, however, a method to extract the diesel residue from the charred debris was investigated. Of the ILR extraction procedures maintained by ASTM, passive headspace using activated charcoal is more commonly used [9]. However, because it is a headspace method, it can be biased against heavier, less volatile components. Diesel is considered a heavy petroleum distillate because it contains high carbon number compounds; therefore a headspace method has the potential to disproportionately extract the less volatile diesel components. For this reason, a solvent extraction is the preferred extraction method for diesel and thus was selected as a more representative procedure.

Via preliminary studies, the solvent extraction method chosen was to add 5 mL of carbon disulfide (CS_2, spectrophotometric grade, Sigma-Aldrich, St. Louis, MO) to the matrix to be extracted in a 50 mL round bottom flask, which was then attached to the rotary arm of a Rotovap (R110, Büchi, Switzerland). The arm, which during normal operation of the Rotovap sits in a heated water bath, was positioned outside the water bath to prevent evaporation. The rotary function was adjusted to a setting of 4 out of 10, and the extraction mixture was allowed to agitate for 5 minutes. The solvent was then removed with a glass Pasteur pipet and, if necessary, filtered through a disposable syringe (Becton Dickinson & Co., Franklin Lakes, NJ) with a 25 mm, 0.2 μm pore size PTFE membrane syringe filter (Grace Davison Discovery Sciences, Deerfield, IL). The filtrate

was then analyzed by GC-MS using the same temperature program and instrument parameters described previously (Section 4.2.1).

In order to demonstrate the efficiency of the solvent extraction method, a spike and recovery study was performed for the three matrices (cotton cloth, magazine, and carpet) to be considered in the burned studies. The cotton cloth was taken from a white cotton wash cloth (100% cotton, Wholesale Merchandisers, Grand Rapids, MI). The magazine was cut from a copy of ESPN The Magazine (20 pages including cover and glossy pages, ESPN, New York, NY). The carpet was taken from a roll of unused nylon carpeting (origin unknown). A series of standard solutions containing 1,3,5-trimethylbenzene (98%, Aldrich, Milwaukee, WI), decane (99+%, Aldrich, Milwaukee, WI), indane (97%, Aldrich, Milwaukee, WI), dodecane (99+% olefin free, Matheson, Coleman, & Bell, Norwood, OH), and tetradecane (99%, Aldrich, Milwaukee, WI) were prepared in dichloromethane (CH_2Cl_2, spectrophotometric, Sigma-Aldrich, St. Louis, MO) at different concentrations: 0.01 %, 0.03 %, 0.05 %, 0.07 %, and 0.10 % (v/v). These components were selected to represent the common compounds classes present in diesels that span the retention time range. One mL of each calibration standard was first spiked with no matrix present, *i.e.* straight into the round bottom flask. It was then subjected to the extraction procedure as if a matrix were present and analyzed by GC-MS. The peak areas were integrated using the ChemStation software (Agilent, Santa Clara, CA) and plotted against mass injected (calculated using density) to create a calibration curve for each component in the calibration standard. The same extraction procedure was then performed with the matrix present for all concentrations of the calibration standard solutions. The mass of each component recovered was determined

by substituting the corresponding peak area into the appropriate calibration equation. The calculated mass was then divided by the theoretical mass in order to determine a percent recovery and hence assess the efficiency of the extraction procedure for each component at each of the spiked concentrations.

4.3.2 Results and Discussion

The first spike and recovery study was performed for the cotton cloth matrix. The calibration curve for the neat standards by mass injected (no matrix present) is shown in Figure 4.7 for all five components of the calibration standard. All five linear regressions show R^2 values of greater than 0.9900. Table 4.5 shows the percent recovery values of each calibration standard from the cloth. With the exception of the 0.01% (v/v) standard solution, all recovery values are approximately 90% with a standard deviation of less than 0.5%. The higher than average recovery for the 0.01% (v/v) standard is most likely due to the fact that it is at the lower end of the linear range, where the theoretical mass to be recovered is already small. In fact, the linear regression equations alone nominally accounted for a significant portion of the recovery because the x-intercept values for each were close to the theoretical recoveries for the 0.01 % (v/v) standard. It should also be noted that the low standard deviations for each calibration standard indicate that the solvent extraction procedure does not preferentially extract one type of component.

Figure 4.8 shows the calibration curves for the neat standards by mass injected (no matrix present) prepared for the day in which recoveries were examined for the magazine matrix. Again, R^2 values of greater than 0.9900 indicate a linear calibration curve for the standard solutions. Table 4.6 lists the recovery values for each calibration standard from the magazine. Similar trends to the cloth recovery values are observed.

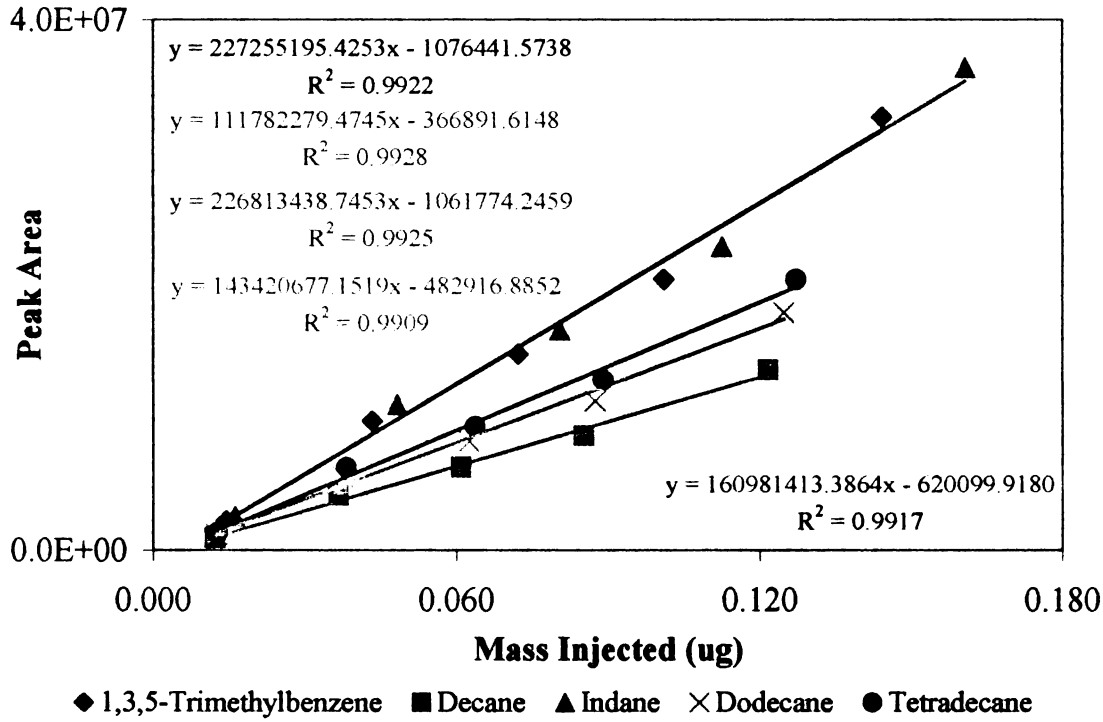

Figure 4.7 Calibration Curve for the Neat Calibration Standards for Cloth Matrix Recovery Study

Table 4.5 Extraction Recoveries from Cloth for Each Calibration Standard (1,3,5-TMB = 1,3,5-trimethylbenzene, C10 = decane, C12 = dodecane, C14 = tetradecane)

Standard Concentration	Percent Recovery					Average Recovery
(% v/v)	1,3,5-TMB	C10	Indane	C12	C14	(%)
0.01	106.33	101.89	105.16	101.27	101.76	103.28 ± 2.30
0.03	87.86	87.92	87.54	87.27	87.19	87.56 ± 0.33
0.05	87.65	88.29	88.02	88.33	87.71	88.00 ± 0.31
0.07	87.35	87.96	88.11	87.26	87.21	87.58 ± 0.42
0.10	92.97	93.09	92.78	92.97	93.00	92.96 ± 0.11

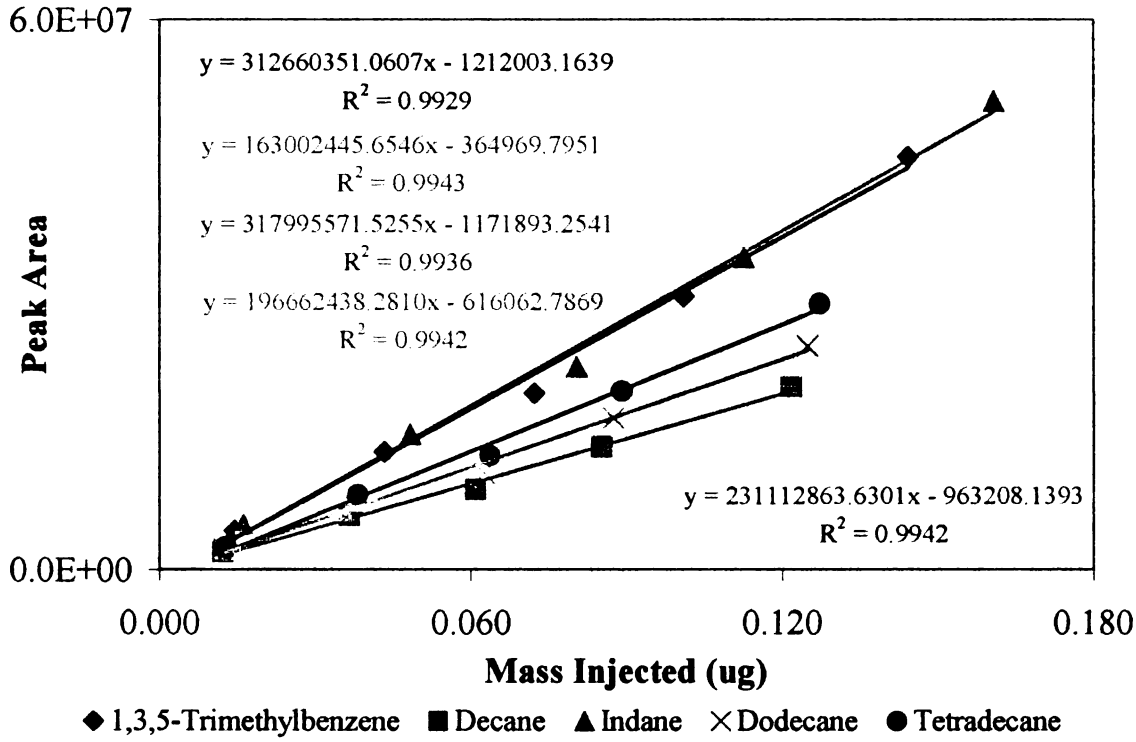

Figure 4.8 Calibration Curve for the Neat Calibration Standards for Magazine Matrix Recovery Study

Table 4.6 Extraction Recoveries from Magazine for Each Calibration Standard (1,3,5-TMB = 1,3,5-trimethylbenzene, C10 = decane, C12 = dodecane, C14 = tetradecane)

Standard Concentration	Percent Recovery					Average Recovery
(% v/v)	1,3,5-TMB	C10	Indane	C12	C14	(%)
0.01	115.78	111.98	114.44	110.62	116.21	113.81 ± 2.43
0.03	98.35	97.74	97.85	98.28	99.53	98.35 ± 0.71
0.05	86.35	86.66	85.83	86.38	87.29	86.50 ± 0.53
0.07	104.22	105.04	104.54	105.56	106.04	105.08 ± 0.74
0.10	99.13	99.95	99.51	99.86	100.54	99.80 ± 0.52

The 0.01% (v/v) standard is higher than average, while the rest of the standards show recoveries all greater than 85%. Even though the recovery value for the 0.07% (v/v) standard is slightly higher than 100%, it still falls within an acceptable range for recoveries (5% error, or a range of 95-105% recovery) [38]. As before, the low standard deviations indicate no compound bias in the solvent extraction procedure from the magazine matrix.

Figure 4.9 shows the calibration curves for the neat standards by mass injected (no matrix present) prepared for the day in which recoveries were examined for the carpet matrix. R^2 values are also above 0.9900 for the linear regression equations. Table 4.7 lists the recovery values for each calibration standard from the carpet matrix. Again, the same trends as for the cloth and magazine are observed. In this instance, however, the recovery value for the 0.05% (v/v) standard is low by comparison with other recovery values. In the corresponding calibration curves, however, it appears that the peak areas for the 0.05% (v/v) standard are lower than the expected peak areas determined by the regression equations. It is possible that the standard was poorly prepared. It could have been omitted from the calibration curve entirely, but because acceptable R^2 values were still attained, the 0.05% (v/v) standard values were retained even with the disparity. Since the same standard that was used for the neat calibration curve was also used for the spike and recovery from the matrix, it is feasible that, if poorly prepared, this standard would project low in the recovery rates as well.

The results of the spike and recovery studies using a representative standard solution indicate that a five minute extraction by agitation in five mL CS_2 is likely to be sufficient for the extraction of diesel from the three matrices investigated. The recoveries

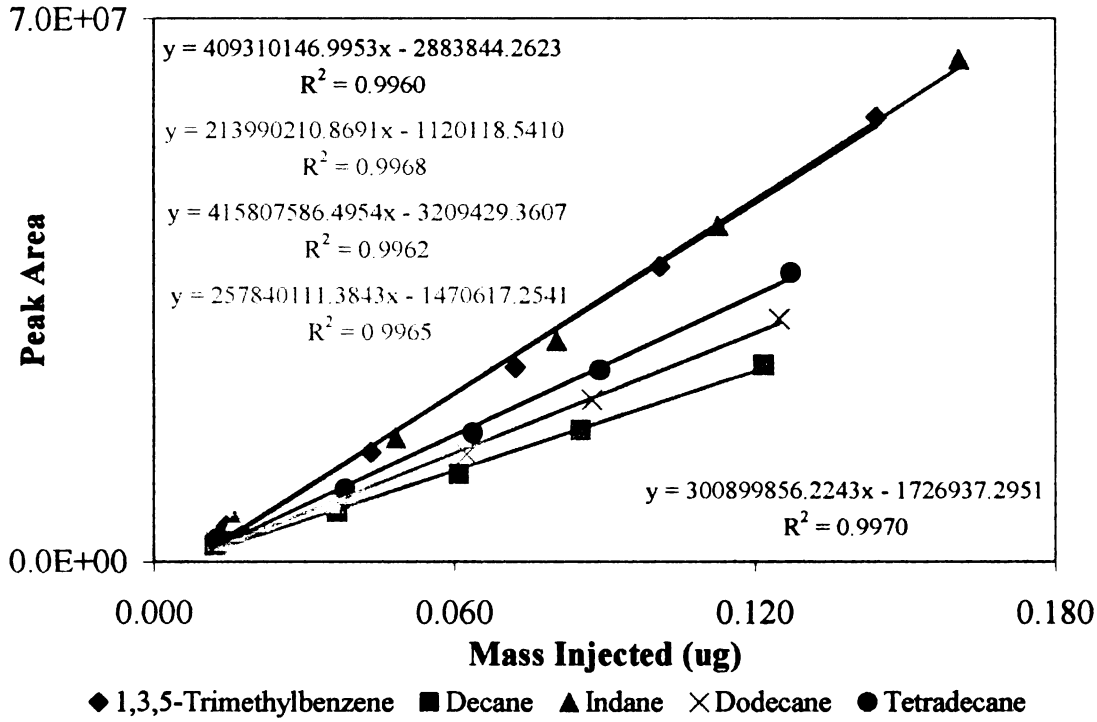

Figure 4.9 Calibration Curve for the Neat Calibration Standards for Carpet Matrix Recovery Study

Table 4.7 Extraction Recoveries from Carpet for Each Calibration Standard (1,3,5-TMB = 1,3,5-trimethylbenzene, C10 = decane, C12 = dodecane, C14 = tetradecane)

Standard Concentration (% v/v)	Percent Recovery					Average Recovery (%)
	1,3,5-TMB	C10	Indane	C12	C14	
0.01	135.02	133.22	136.10	137.25	138.01	135.92 ± 1.89
0.03	97.39	98.13	97.37	99.53	100.41	98.57 ± 1.35
0.05	73.40	74.78	73.10	75.29	75.55	74.42 ± 1.11
0.07	90.72	92.25	89.77	92.84	93.43	91.80 ± 1.52
0.10	81.68	82.39	80.34	83.43	84.20	82.41 ± 1.50

are certainly not optimal; however, they are adequate for the purposes of this research project, especially since fire debris analysis is typically qualitative and not quantitative in nature. The more important feature of the solvent extraction procedure is that it is not biased toward any particular component or compound class in diesel, as any preference would skew the results of the PPMC coefficients and the PCA. Due to the sufficiency of the results of the spike and recovery studies, the solvent extraction procedure was deemed appropriate for subsequent extractions of spiked diesels from burned matrices.

4.4 Analysis of Burned Diesels

4.4.1 Procedure

Three matrices (cotton cloth, magazine, and carpet) were investigated for the extraction and analysis of burned diesels. Each matrix was subjected to a series of burning conditions, with and without diesel present, in order to examine the matrix interferences and burning effects on the diesels. All substrates were cut to three centimeter squares, placed in a glass petri dish, spiked with diesel as necessary, and then burned. All GC-MS analyses were performed using the previously described NCFS.M method.

First, the unburned matrix was extracted using the solvent extraction procedure and analyzed in order to identify the presence of any potential interferences inherent to the matrix itself. Next, the matrix was burned, extracted, and analyzed to determine any pyrolysis products created during the burning process that could also act as potential interferences. To burn the matrix, a butane grill lighter (BIC, Shelton, CT) was used to ignite it, and it was allowed to burn until self-extinguished. If after extinguishing, the majority of the surface was not charred, the substrate was re-ignited until significant

charring had occurred. Next, 50 μL of Diesel 21 was spiked onto the unburned matrix, which was then extracted and analyzed in order to examine recovery of the diesel and potential interferences. The same conditions were repeated for a burned matrix, *i.e.* the diesel was spiked onto the burned matrix, in order to assess the efficiency of the diesel recovery from the burned matrix. The final conditions examined were those most similar to an actual arson case. Diesel 21 was spiked, again 50 μL, onto the matrix, which was then ignited. The debris was extracted and analyzed by GC-MS in order to assess the potential for the association of the burned diesel to its unburned counterpart.

After Diesel 21 was used to carry out each burning series for all three matrices, two other previously analyzed samples were treated as blind unknowns and analyzed in an attempt to assess the potential for the association of a burned diesel extracted from fire debris to its unburned counterpart. A colleague selected two diesels and placed them in vials labeled "A" and "B". These two blind samples were then spiked (50 μL) onto each of the three matrices, burned, and finally extracted and analyzed by GC-MS.

For the data sets collected for this portion of the research, the need for data pre-treatment is the same as described before, though some minor adaptations were necessary to accommodate the alterations to the chromatograms effected by both the burning process and the extraction procedure, such as loss of volatiles and variation in extraction efficiency. The TICs from the burned diesel data set (the samples that were spiked onto the unburned matrix and then burned) were similarly compiled and retention time aligned, though a window size of five was insufficient for their alignment (the algorithm failed with a window of five). For that reason, the burned TIC data set was aligned using a window size of seven. Targets were selected at random for each data set. The EIPs

were similarly compiled and aligned. For some EIPs, the same parameters used to align the TIC were sufficient for alignment. However, other EIP sets required a manual selection of the noise threshold for peak identification as opposed to using the default calculation applied by the alignment algorithm. Both the indane and PNA profiles required a threshold of 100, while the OCP profile required a threshold of 300. Normalization and mean-centering were also performed in the same manner as detailed in Chapter 3, though each data set was treated separately. For example, the burned diesels were normalized and mean-centered separately from the neat diesels. Separate treatments were necessary because of the differences in abundances between a 1:10 dilution of a neat diesel and an extracted 50 μL diesel spike that had been burned.

After pre-treatment, the TICs and EIPs were then analyzed as described in Chapter 3. PPMC coefficients were used to determine the level of correlation among sample pairs. PCA was performed in order to observe the natural clustering of the diesels based on chemical composition. It should be noted that PCA was not actually performed on the burned diesels. Instead, the eigenvectors calculated for the neat diesel data set were used because they represent the chemical components that are the sources of maximum variance among the five diesels. The eigenvectors were used to calculate a score for the diesels that were extracted from the burned matrices. This score was calculated in Microsoft Excel by multiplying each point in the eigenvector by its respective point in each mean-centered chromatogram. These products were then summed to calculate the score for that diesel corresponding to that specific principal component. The objective was to associate and discriminate the samples based on their chemical composition, not on changes introduced in the burning and extraction process.

If the diesels from the burning trials were included in the PCA, then the PCA would specifically search for any differences among the neat and burned samples instead of associating and discriminating them only on their inherent composition.

4.4.2 Results and Discussion

4.4.2.1 Assessment of Potential Interferences from Unburned and Burned Matrices

Figure 4.10 shows sample chromatograms from the extraction of the three unburned matrices. In the cloth matrix, no peaks of interest were observed—in fact, the chromatogram resembled that of a blank solvent injection. In the magazine extract, however, a relatively significant peak eluted at approximately 16 minutes. A mass spectral library search tentatively identified this peak as a long chain ester, likely from the ink used to print the magazine. Other peaks at lower abundance are also present in the unburned magazine. In the carpet extract, two significant peaks were observed after 20 minutes. Mass spectral library searches indicated that these two peaks were bi-naphthalene products, potentially from the carpet backing, adhesives, or a chemical treatment such as water repellant or stain resistant. Again, smaller peaks are also observed throughout the chromatogram. These smaller peaks, however, are at such an insignificant abundance compared to the abundances expected for the diesel components; therefore, it is unlikely that these smaller matrix peaks will interfere in anyway with the results of the chemometric procedures.

Figure 4.11 shows sample chromatograms from the extraction of the three burned matrices. Again, the cloth extract contains no significant peaks. The magazine and carpet extracts contain the same peaks as observed in the unburned extracts, though at higher abundance. These increased levels could be due to variation in the extraction

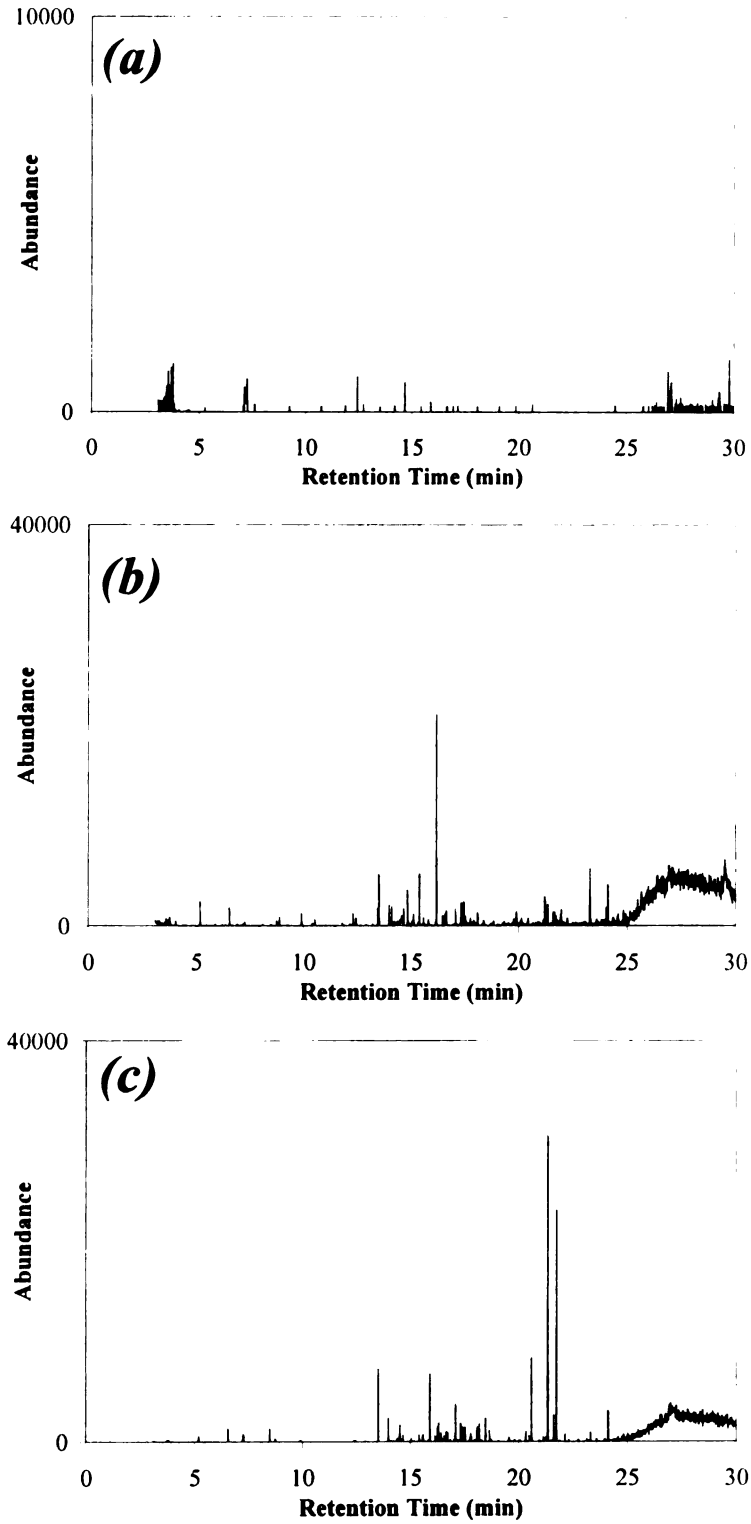

Figure 4.10 Representative Chromatograms of Unburned Matrices: (a) Cloth, (b) Magazine, and (c) Carpet

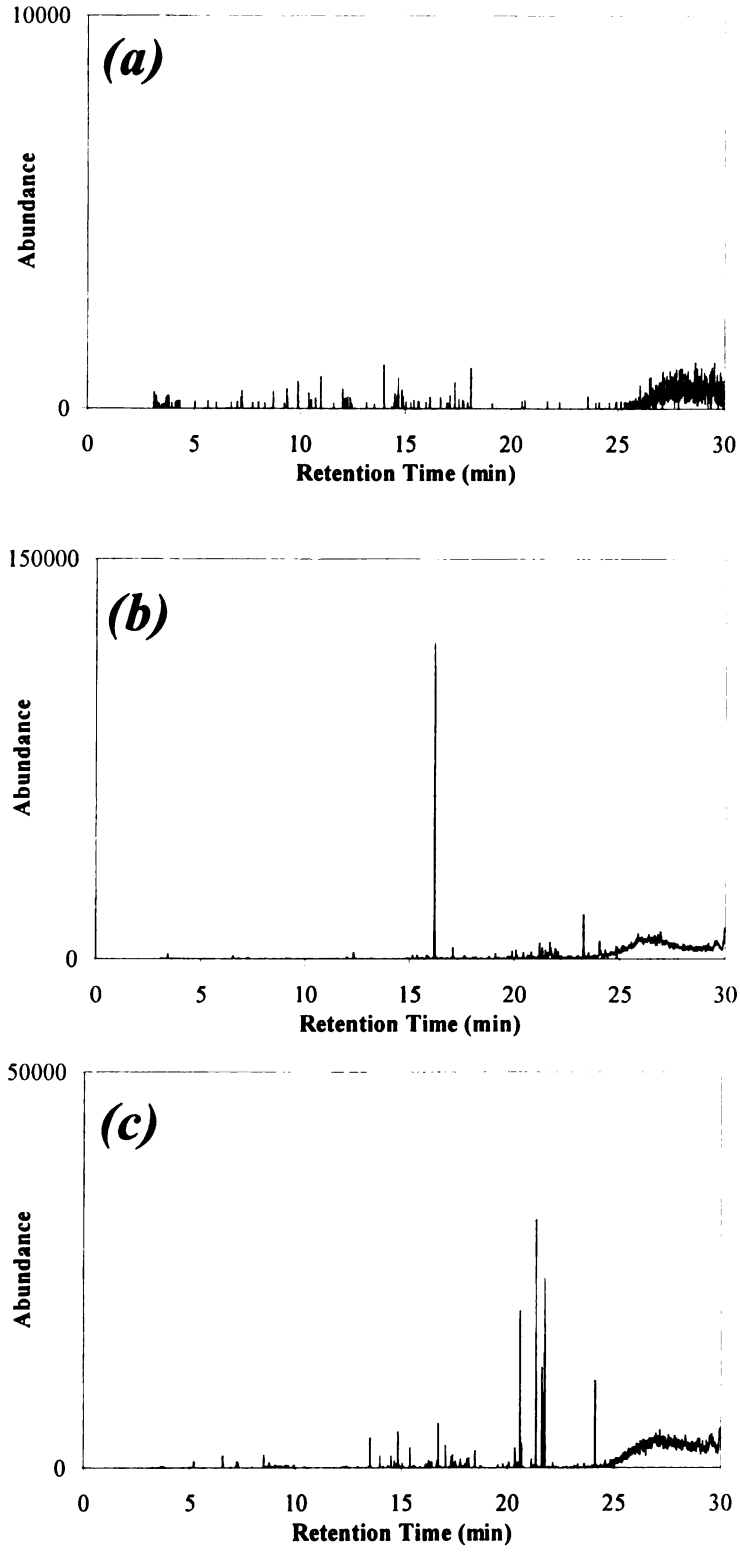

Figure 4.11 Representative Chromatograms of Burned Matrices: (a) Cloth, (b) Magazine, and (c) Carpet

efficiency, or even differences in injection volume. It is possible that these peaks could interfere in the chemometric results if they remain significant in abundance in comparison to the presence of a diesel sample.

It should be noted that no significant peaks that could be attributed to pyrolysis products (that is, peaks present in the burned matrix but not in the unburned) were observed for any of the three matrices. It is possible that pyrolysis product formation is limited in these three matrices, or again that the pyrolysis products are volatilized and lost to the environment during the burning process. It is also possible that the solvent extraction procedure is not selective for any pyrolysis products present, *i.e.* the pyrolysis products may not be soluble in the solvent. Whatever the reason, the lack of interfering pyrolysis products is advantageous for the accuracy of the results of both the PPMC coefficients as well as PCA.

4.4.2.2 Solvent Extraction of Diesels from Unburned and Burned Matrices

Figure 4.12 shows sample chromatograms from the extraction of the three unburned matrices spiked with 50 μL of Diesel 21. All three chromatograms show similar diesel chromatographic patterns. No extraneous peaks are observed that could potentially interfere with the chemometric results. Figure 4.13 shows sample chromatograms from the extraction of the three burned matrices spiked with 50 μL of Diesel 21. Again, a similar chromatographic pattern is observed, and no interference peaks are obvious. The lack of any interference peaks in either the unburned or burned matrices indicates that the diesel is present at a sufficient concentration that inherent hydrocarbons from the matrices do not make significant contributions to the chromatograms. The consistency in the diesel peak pattern from the extracts of both

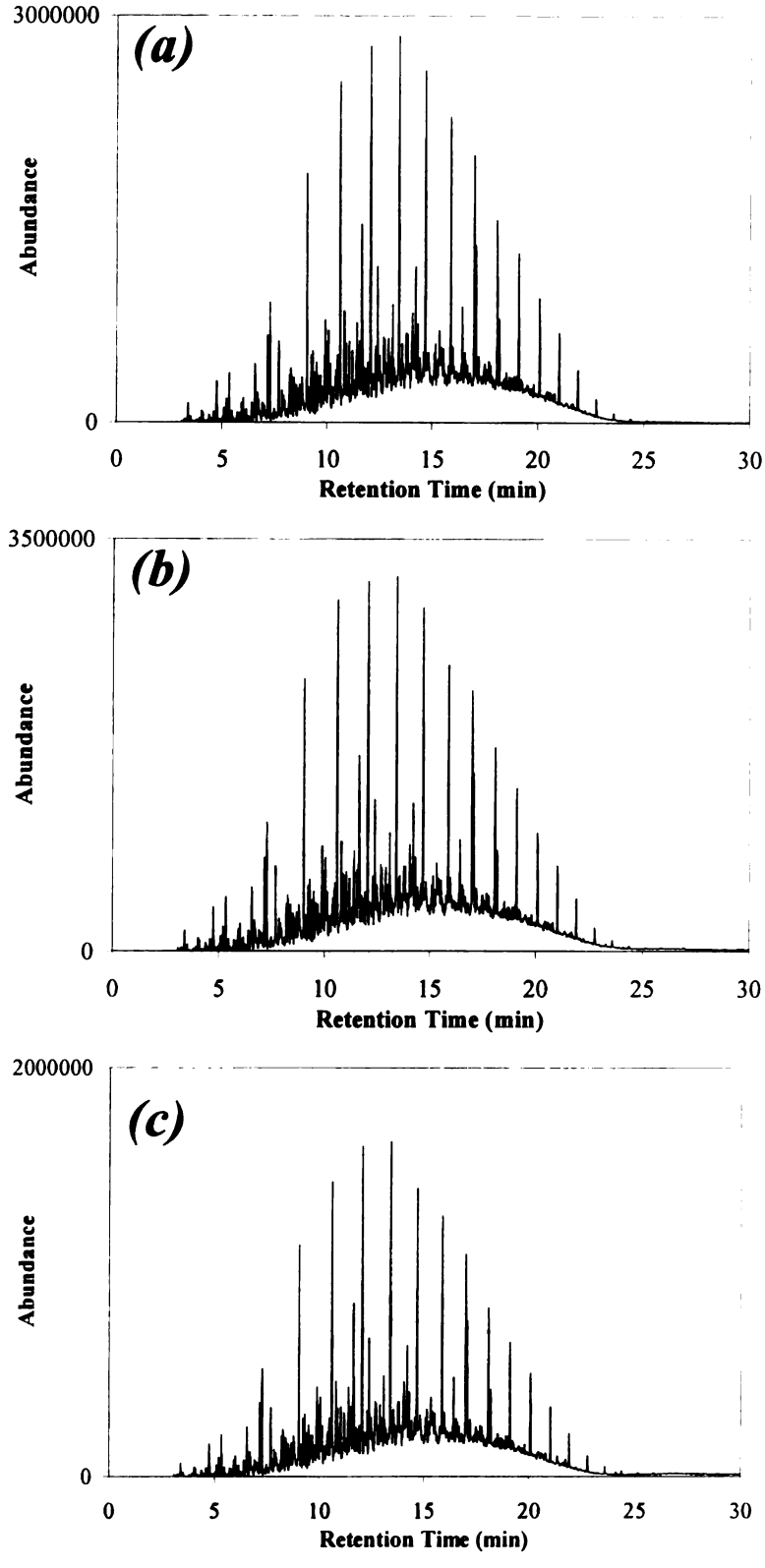

Figure 4.12 Representative Chromatograms for Unburned Matrices Spiked with Diesel 21: (a) Cloth, (b) Magazine, and (c) Carpet

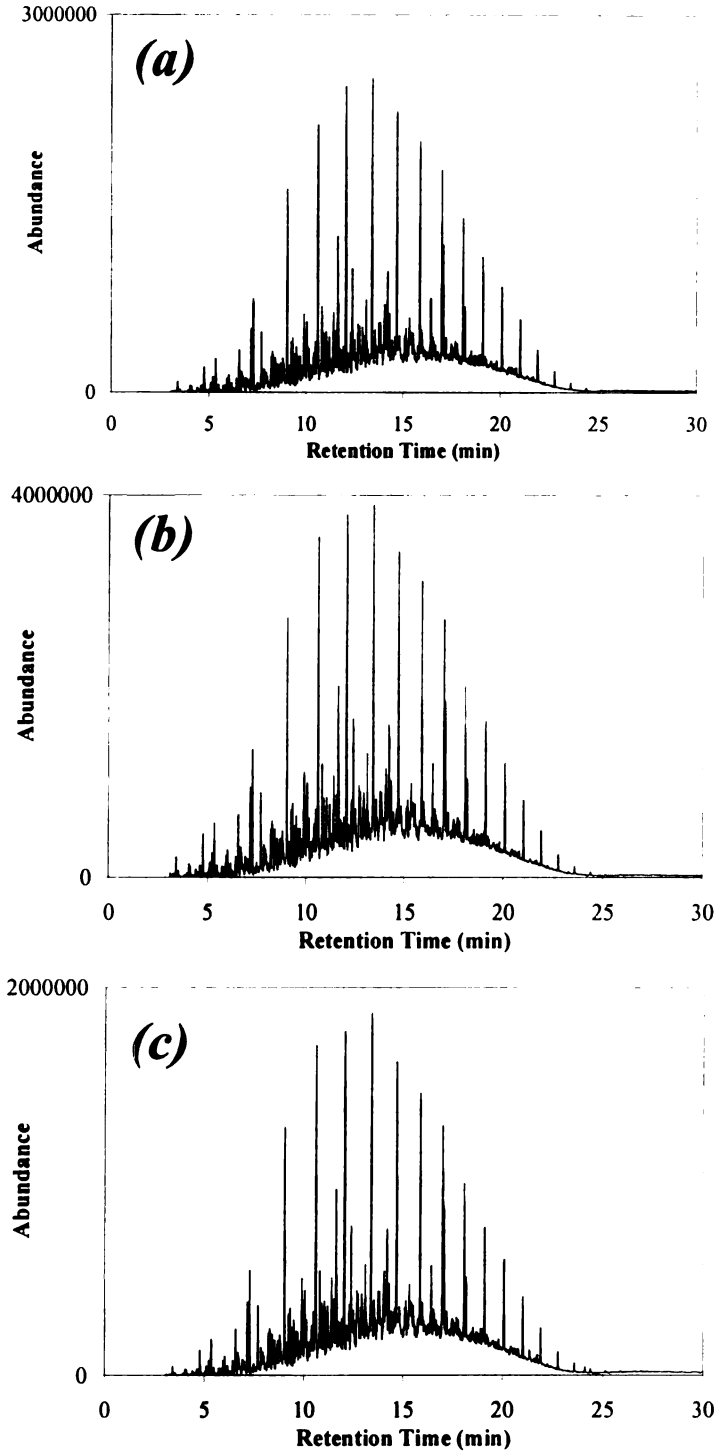

Figure 4.13 Representative Chromatograms for Burned Matrices Spiked with Diesel 21: (a) Cloth, (b) Magazine, and (c) Carpet

burned and unburned matrices also signifies that the presence of the matrix does not negatively affect the solvent extraction of the broad range of diesel components.

4.4.2.3 PPMC Coefficients of Neat and Burned Diesels

Sample chromatograms for the extraction of spiked and burned diesels from each of the three matrices are shown in Figure 4.14. PPMC coefficient tables for the compiled neat and burned data can be found in Appendix D. For the TIC PPMC coefficients, the burned Diesel 21 replicates (spiked on unburned matrix, then burned) were assessed for precision of the burning process for all three matrices. The average correlation coefficient for each matrix was as follows: cotton cloth – 0.9847, magazine – 0.9344, and carpet – 0.8411. These correlations, which are lower than observed for neat diesel replicates, indicate the degree of uncertainty introduced by the burning process, which appears to be matrix dependent. The cotton cloth yields higher PPMC coefficients for Diesel 21 when it is burned and extracted in comparison to the other two matrices. The higher level of correlation for cotton cloth indicates that either the burning process is more reproducible for the cloth matrix, or that the solvent extraction procedure is the most efficient for diesel from the cloth. The replicate spiked and burned extracts from the magazine are less correlated, most likely because of the way the magazine itself burns. Unlike the cloth, which only chars, the magazine becomes ashen. This difference makes the surface area of the burned matrix variable, and thus introduces variability in the PPMC coefficients. The magazine is also less absorbent than the cloth, and is less apt at shielding the diesel from the burning process. The carpet yielded the least precise correlation coefficients for the replicate spiked and burned extracts of Diesel 21. This imprecision is most likely due to the relatively high retention of the diesel by the carpet.

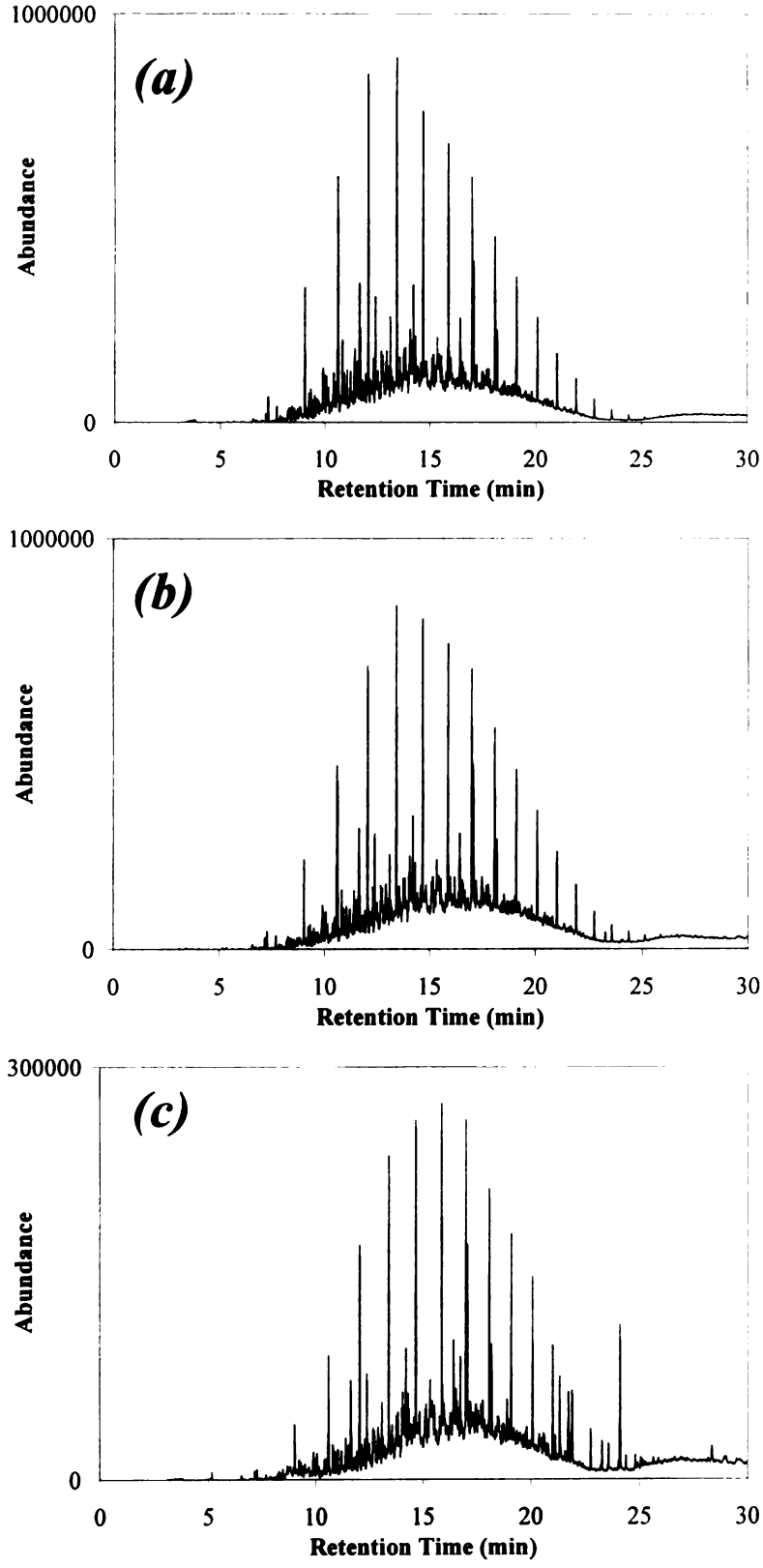

Figure 4.14 Representative Chromatograms for Matrices Spiked with Diesel 21 and then Burned: (a) Cloth, (b) Magazine, and (c) Carpet

This increased retention may protect the diesel from the fire, but it can also hinder the solvent extraction procedure. The carpet also has a greater surface area than the two other matrices due to the height of the carpet fibers from the carpet backing, as well as the presence of multiple fibers. This additional surface area can lead to a more variable burning process. The difficulty in extraction and imprecision in the burning process may prevent replicate burnings of diesel on carpet from being precise.

In addition, PPMC coefficients were utilized to associate the burned Diesel 21 to its neat counterpart. However, the highest correlation for none of the three matrices corresponded to Diesel 21. The cloth extracts were on average more closely associated with Diesel 23 (0.8840) than Diesel 21 (0.8657), the magazine extracts from the magazine with Diesel 25 (0.8183) instead of Diesel 21 (0.7977), and the carpet extracts with Diesel 22 (0.6203) instead of Diesel 21 (0.6028). These differences, however, are not statistically significant at the 90% confidence level, which indicates that the extracts are as well correlated with Diesel 21 as with the other neat samples. Several steps were taken in order to improve the correlation coefficients between Diesel 21 and the three matrix extracts, which included the selection of different target chromatograms for the alignment algorithm, the alteration of the user defined window size for the alignment algorithm, and the statistical examination of replicate samples for outliers. These changes, however, did not affect the trends observed for the correlation coefficients calculated for the matrix extracts.

For the blind samples, it should first be noted that the correlations for the TICs of the magazine and carpet extracts for Blind B (Appendix D) are all either poor or negative, which indicates a complete lack of correlation to any of the neat diesels. It is possible

that these samples are insufficient for comparison due to poor recovery by the solvent extraction procedure. The cloth extract for Blind B has highest average correlation with Diesel 25 (0.9076). The three extracts for Blind A all have maximum correlations with Diesel 22 (cloth – 0.8665, magazine – 0.8575, and carpet – 0.8339). This regularity in maximum correlation indicates that Blind A is most consistent with Diesel 22.

Closer examination of the PPMC coefficients for the EIPs reveals similar trends to those observed in the TIC. The burned Diesel 21 extracts are somewhat correlated with neat Diesel 21. However, extracts from all three matrices for Blind A consistently have a maximum correlation with Diesel 22, and the cloth extract for Blind B consistently maximizes when paired with Diesel 25.

The PPMC coefficient results for the burned diesels indicate that the burning process itself is highly variable. This variability inevitably affects the precision of the PPMC coefficients and can impede the association of burned diesels to their unburned counterparts. This variability also seems to be dependent on the features of the matrix being burned, which include how the burning affects the surface area of the matrix, and how the matrix retains the diesel and shields it from the heat of the fire. On the other hand, a consistency was observed for the maximum correlations of the blind diesel samples to a neat diesel sample, which implies that some amount of association is still possible even after the effects of the burning process, even though association was not demonstrated for the replicates of Diesel 21.

4.4.2.4 PCA of Neat and Burned Diesels

Initially, the burned data was concatenated with the neat data, all of which was carried through the previously described data pre-treatment processes. The mean-

centered data was then subjected to PCA and a scores plot generated for the TICs. This scores plot, shown in Figure 4.15, demonstrates the data set dependency of the PCA procedure. PCA is designed to calculate the variance among the given data set. PCA as an unsupervised procedure is incapable of associating a neat diesel and one that has been altered during burning based on chemical composition, because obvious differences exist between those chromatograms. In the scores plot, the neat diesels are clustered on the negative side of PC1, while the burned diesels are clustered on the positive side. Thus, PCA is not a feasible option for a compilation of neat and burned samples.

When considering PCA as an associative and discriminatory tool, the nature of the samples to be associated and discriminated must be determined. In this research, the objective is two-fold: to discriminate burned diesels of different origin from one another, and to associate burned diesels to their unburned counterparts. In order to achieve this objective, the factors that are capable of associating and discriminating neat diesels based on chemical composition (*i.e.* the eigenvectors from the neat diesel PCA) can also be applied to burned diesels from the same data set in order to associate and discriminate them based on chemical composition. The assumption is that sufficient significant features of the diesels persist through the burning process to still associate and discriminate them based on the eigenvectors calculated for the neat diesel set. It is also possible that a specific compound class is more likely to remain after burning, so that the EIPs may provide more discriminatory information than the TIC alone.

Once the scores were calculated for the first two principal components for all the burned samples for the TIC and the EIPs, they were added to the scores calculated for the neat diesel set, and a new scores plot was generated. Each blind sample was consolidated

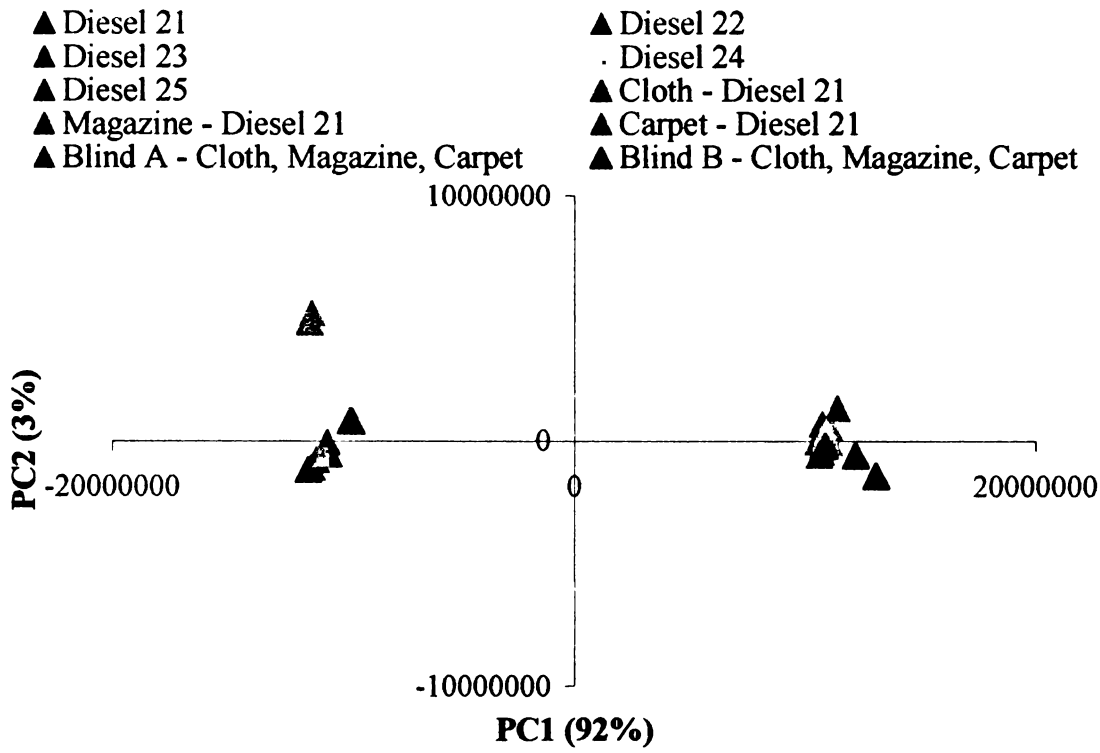

Figure 4.15 Scores Plot for the TIC of the Neat and Burned Diesels

into a set of scores for all three matrices. However, an initial assessment of the resulting scores plots indicated that the scores for the burned diesels all seemed to center around the origin. Exemplary scores plots for the TIC and alkane EIP can be found in Figure 4.16. It was first thought that this location of the scores for the burned data was indicative of a lack of chemical features in the burned chromatograms. However, a closer look at the scores calculation method revealed that significant disparity in relative abundances between the neat and burned diesels would lead to a difference in the magnitude of their respective scores values. More explicitly, the eigenvectors were calculated for the normalized abundances of the neat diesels. These same eigenvectors were then multiplied by the less abundant chromatograms of the burned diesels and summed to calculate a score. Therefore, these scores were lower in magnitude based on the differences in abundances between the neat and burned diesels.

This discovery is an important revelation when considering the applicability of this method to actual arson cases. It seems some method of correction is necessary for samples that differ greatly in abundance levels in order to apply pre-determined eigenvectors to calculate scores. In this case, it appeared that the neat diesel chromatograms were approximately an order of magnitude larger in abundance than the burned diesel chromatograms, so a correction factor of ten was applied. The normalized burned data was multiplied through by ten, and the data was again mean-centered and the scores calculated. It was observed that this multiplication of ten to the normalized data led merely to an approximate ten-fold multiplication of the calculated scores values, so henceforward the already calculated scores were simply multiplied through by ten. The score plots were re-generated, and observations were made about their probative value

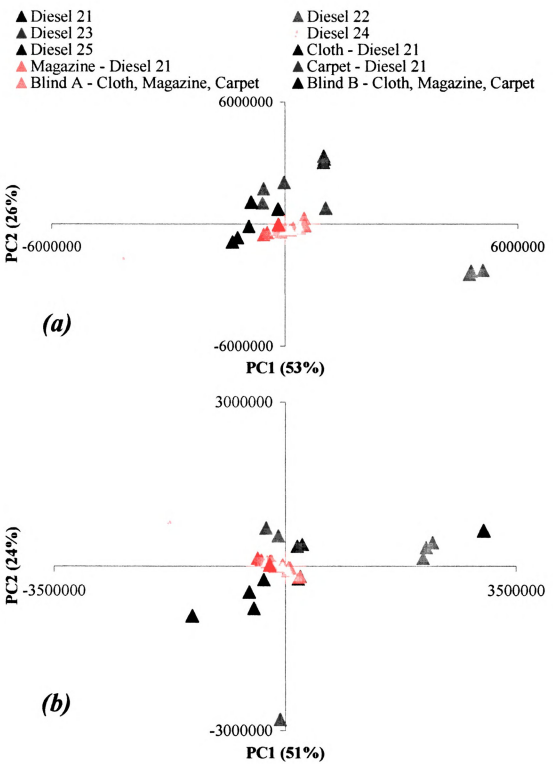

Figure 4.16 Representative PCA Scores Plots for (a) TIC and (b) Alkane EIP for the Burned Data Scored with the Eigenvectors from the Neat Data

for the association and discrimination of the neat and burned diesels.

Figure 4.17 shows the TIC scores plot containing the neat and burned diesels. The first observation is the obvious spread in the replicates of the burned diesels as compared to the replicate analyses of the neat diesels. The spread occurs in both PC1 and PC2, and because these eigenvectors correspond to actual chemical differences as suggested by the discrimination of the neat diesels, it is likely that the spread in the replicates is caused by genuine dissimilarities in their chromatograms. These discrepancies can be attributed to variability in both the burning process and extraction efficiency; therefore, any interpretation of the association and discrimination among samples must be prefaced with this potential for variability.

The scores for Diesel 21 spiked onto the three matrices and extracted are only moderately close to the scores for neat Diesel 21. Two replicates of Diesel 21 spiked onto a magazine and burned are more closely associated to the neat diesel than those extracted from the other two matrices, though one cloth replicate is close as well. The carpet replicates are not remotely close to the neat diesel. This trend is sensible, as the magazine is less absorbent than the cloth and carpet matrices. Neither of the blind samples can be logically associated with a specific neat diesel cluster. For Blind A, the carpet extract is located in the proximity of the Diesel 22, which is consistent with the PPMC coefficients results, while the magazine extract is closer to the Diesel 21 cluster. The cloth extract is located between the other two extracts and cannot reasonably be associated with any neat diesel cluster. For Blind B, the cloth extract is located within the cluster for Diesel 21, which is inconsistent with the PPMC coefficients results, while the magazine and carpet extracts are far from any neat diesel cluster in the upper left

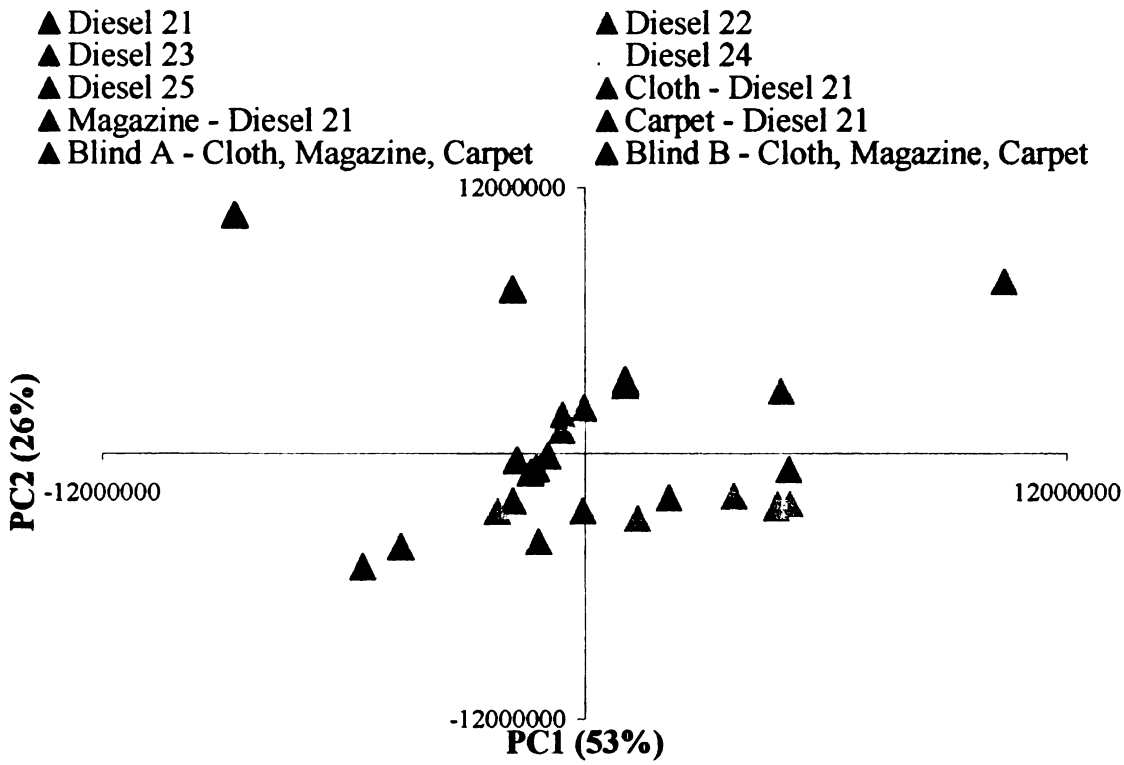

Figure 4.17 Scores Plot for the TIC of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

quadrant of the scores plots.

The alkane scores plot for the neat and burned data, shown in Figure 4.18, exhibits similar traits to those observed in the TIC scores plot. The replicate analyses for burned Diesel 21 are inconsistent and barely associated with their neat counterpart. For Blind A, the cloth and the carpet extracts are associated with the clusters for Diesels 21, 23, and 25, while the magazine extract is more closely linked with Diesel 24. For Blind B, the cloth extract is associated with the Diesel 24 cluster, while the magazine and carpet extracts are again not remotely close to any other clusters. In fact, they are not shown because their scores values are considerably different from the scores values of the rest of the data set.

At this point, it became obvious that the magazine and carpet extracts for Blind B were extremely different from the cloth extract and the rest of the data set being analyzed. An examination of their chromatograms revealed exceptionally low abundances as compared to the other samples. The TIC for the cloth extract of Blind B exhibited an abundance level of approximately 500,000, whereas the TICs for the magazine and carpet extracts exhibited abundance levels of approximately 70,000. The burned samples are already low in abundance, and these aberrant values for the magazine and carpet extracts prevent them from being scored on a similar level as the other samples. It is possible that these two samples were poorly extracted. It does not seem feasible to use a different correction factor for these samples in order to maintain consistency for all the samples throughout the data analysis procedures. Whatever the reason, any interpretation of their association to a neat diesel will henceforth be omitted.

The aromatic scores plot for the neat and burned diesels is shown in Figure 4.19.

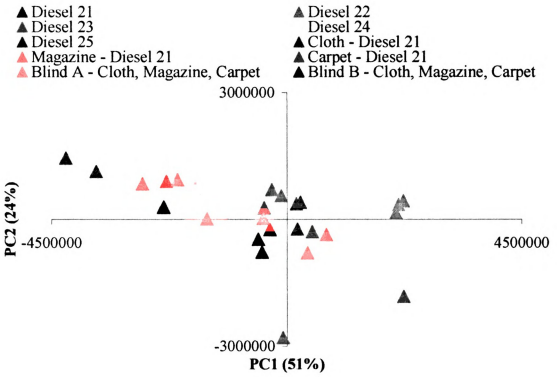

Figure 4.18 Scores Plot for the Alkane EIP of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

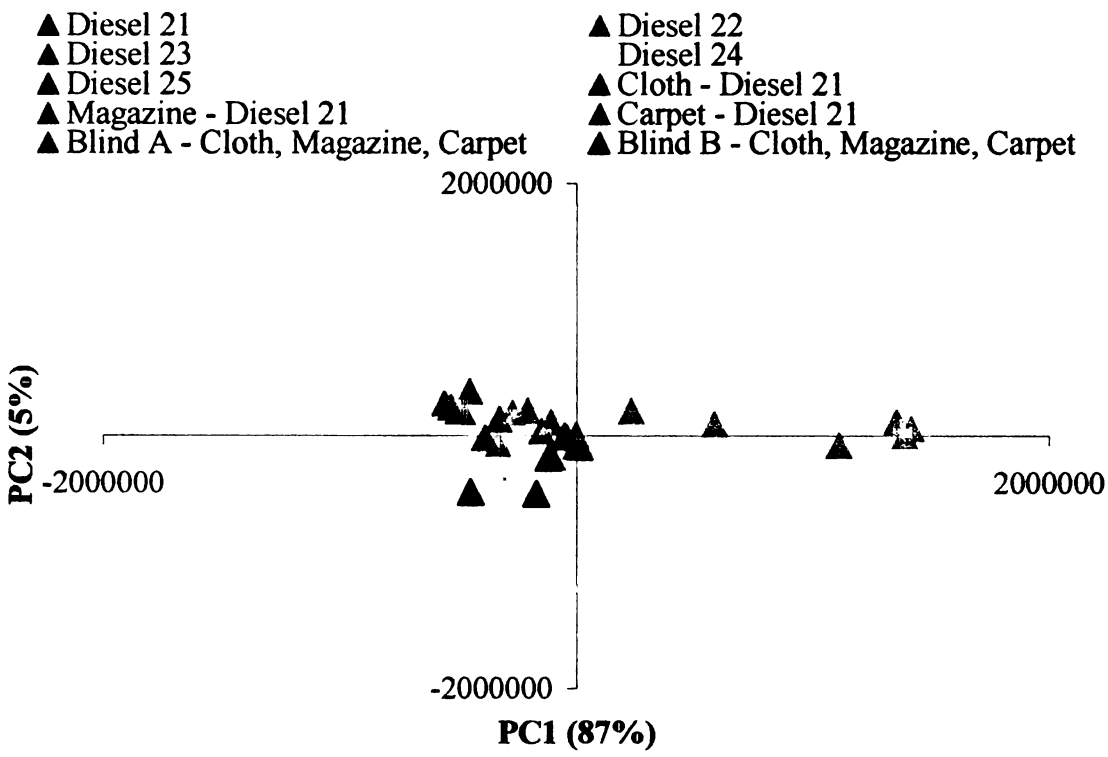

Figure 4.19 Scores Plot for the Aromatic EIP of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

Greater precision among the burned replicates is observed than for the other scores plots, and the burned Diesel 21 scores for all three matrices fall in the four diesel cluster observed in the neat aromatic scores plot that contains Diesel 21 (as well as Diesels 23, 24, and 25). The cloth extract for Blind B also falls in that same cluster, which also contains Diesels 23, 24, and 25. An interesting feature to observe is the location of the scores for the three extracts of Blind A. The three extracts are separated from the four diesel cluster along PC1 toward Diesel 22. The carpet extract is the closest to Diesel 22, while the cloth extract is the furthest away. The relative precision among replicates within this plot suggests that the identity of Blind A is potentially Diesel 22, whereas no reasonable conclusions could be drawn from the other scores plots.

The indane scores plot for the neat and burned diesels is shown in Figure 4.20. As before, significant spread is observed among the burned replicates, though in this case the majority of the spread is along the second principal component. Again, little consistency with the neat sample is observed for the burned Diesel 21 replicates for all three matrices, though the magazine extracts are closest yet again. For Blind A, the extracts from the three matrices are generally closest to the cluster for Diesel 22, though by no means are they close enough to be considered statistically similar. Then again, Diesel 22 is the only neat sample that is positive in PC1, and the Blind A extracts are all significantly positive in PC1; therefore, it is plausible that some degree of association can be suggested by these similarities between the two samples. The carpet extract is once again the closest to Diesel 22. The cloth extract for Blind B is again located in the large four diesel cluster centered about the origin.

The OCP scores plot for the neat and burned diesels is shown in Figure 4.21. The

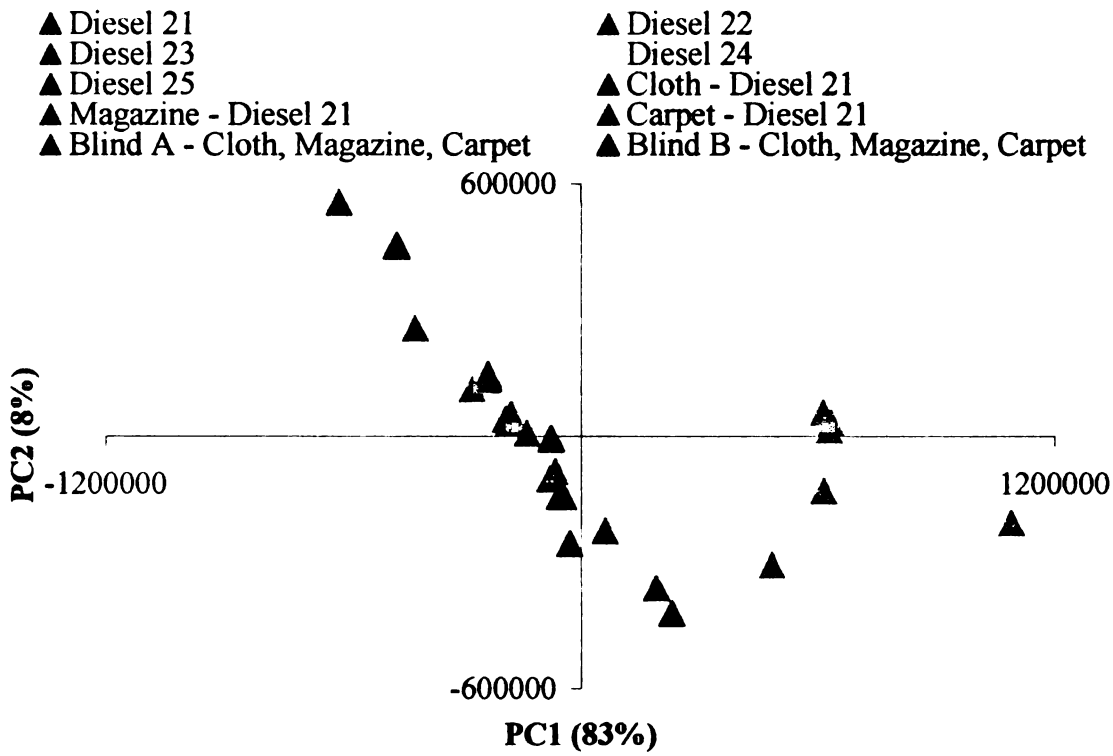

Figure 4.20 Scores Plot for the Indane EIP of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

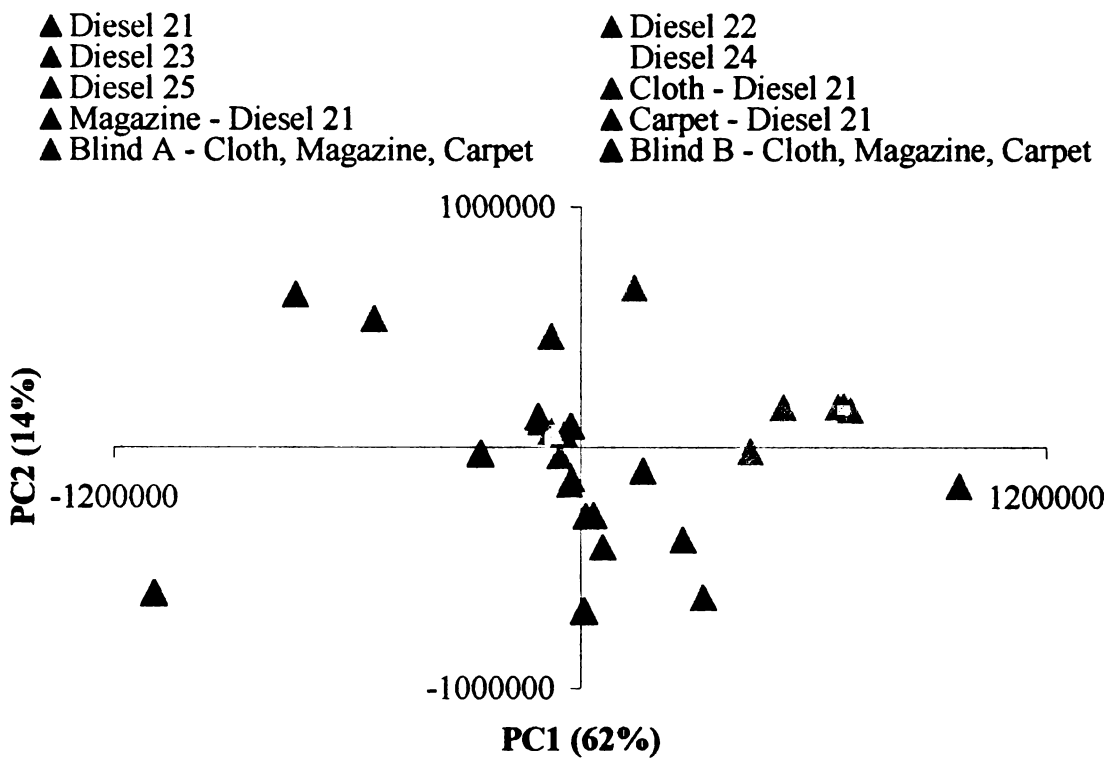

Figure 4.21 Scores Plot for the OCP EIP of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

same trends are observed for the known burned Diesel 21 scores. Few are actually associated with Diesel 21, and the replicate analyses are imprecise as observed by the lack of clustering. The extracts for the three matrices for Blind A are again most closely associated with Diesel 22, with the cloth and carpet extracts located the closest. The cloth extract for Blind B is most closely associated with the clusters for Diesels 21 and 23.

The PNA scores plot for the neat and burned diesels is shown in Figure 4.22, and again the same trends are observed for the known burned Diesel 21 scores. The blind samples, however, are more informative in this plot. The cloth and carpet extracts for Blind A are reasonably associated with the Diesel 22 cluster. The magazine extract is located farther from the Diesel 22 cluster, though it is still negative in PC1, just like the other Diesel 22/Blind A scores and unlike the other neat diesel samples. The cloth extract for Blind B is not associated with any neat diesel cluster.

4.4.2.5 Identification of Blind Diesels

Through the PPMC coefficients and minor corroborating evidence from the PCA scores plots, it was determined that the identity of Blind A was Diesel 22, and that the identity of Blind B was Diesel 25. Although these were the correct assignments, the identifications were not capable of being made with sufficient statistical confidence. Too much variation is present throughout the PPMC coefficients and the PCA results in order to conclusively identify the blind samples. Instead, only the most likely candidates could be determined. However, with the considerable level of variability involved in the extraction procedure and the burning process itself, the identification of a likely candidate among samples that are so inherently similar is useful as a preliminary assessment. The

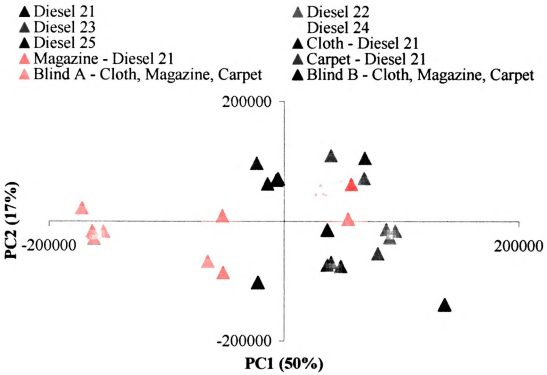

Figure 4.22 Scores Plot for the PNA EIP of the Neat Diesels and the Projected Burned Diesels After a 10X Correction

potential exists for a greater confidence level when associating a burned diesel to its unburned counterpart if diesels were compared with a larger set of different classes of ignitable liquids due to more significant differences in chemical composition.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

5.1.1 Association and Discrimination of Neat Diesels Using PPMC Coefficients and PCA

Throughout the initial analysis of the neat diesel samples, several obstacles were overcome in order to improve the precision of both the analytical method and the chemometric procedures, as well as the significance of the results obtained. It was determined that a two-second timed injection of a one μL sample encased in a μL air pocket is necessary to ensure consistent vaporization of all components in the diesel in the heated injection port. This consistency is imperative to the precision of the injection method. It was also determined that a less dilute sample is essential in order to achieve sufficient abundances in the chromatograms, so as to ensure that any variation in the instrumental background is inconsequential in comparison to the variation among the diesels. However, poor abundances were still observed in some of the EIPs, which indicates that further investigation into the abundance issue is necessary. In addition to a less dilute sample, it was determined that summed EIPs are more informative than a single EIC for improved signal-to-noise.

Once these improvements were applied, a final neat diesel data set was analyzed to investigate the potential for association and discrimination based on chemical composition. PPMC coefficients illustrated that, on a pairwise basis, the diesel samples can either be associated or discriminated based on a comparison of their correlation coefficient to that of replicate samples. The ranges of correlation coefficients for both the replicates and for samples that are different in origin based on EIPs extend further than

those for the TIC, which suggests that the EIPs could provide additional discriminatory information. The PCA results for the TICs demonstrated that the diesels are relatively well differentiated, and that replicate samples are tightly clustered. The PCA of the alkane, indane, and PNA profiles did not provide any additional discrimination capabilities compared to the TIC. It should be noted that errors in the retention time alignment were observed in both the scores plots and the eigenvectors for the aforementioned profiles. These errors cause the results to misrepresent the variation among the samples based on chemical composition alone, so that the discrimination capabilities of these profiles cannot be fairly gauged until these errors are corrected. The PCA results for the aromatic and OCP profiles did, however, offer some additional association and discrimination among the samples. These profiles did not exhibit the same alignment errors as were observed in the alkane, indane, and PNA profiles, which is most likely due to higher abundances and improved peak shapes for the aromatic and OCP EIPs as compared to the other EIPs.

The results from the analysis of this neat diesel data set have shown that it is possible to associate and discriminate diesel samples based on their chemical composition using both PPMC and PCA. The fact that any amount of discrimination is possible among diesels, which are so inherently similar in chemical composition, is significant for the progress of this research. This potential for association and discrimination indicates that it may be possible to apply the same instrumental techniques and chemometric procedures to associate and discriminate diesels that have been burned and extracted from fire debris.

5.1.2 Association and Discrimination of Burned Diesels Extracted from Fire Debris Using PPMC Coefficients and PCA

The objective of this part of the research was to examine the potential of PPMC coefficients and PCA for the association and discrimination of burned diesels that have been extracted from fire debris. In order to accomplish this objective, neat diesel samples were analyzed for comparative purposes. This sample set was analyzed on a new instrument, and it was determined the sensitivity of the new instrument required a dilution of 10:1 instead of 50:1 in order to achieve comparable abundance levels to prior data sets collected on another instrument. It was also determined through RSD calculations and PPMC coefficient determinations that the precision of the neat diesel set was improved over prior data sets. The five diesels in the data set were associated and discriminated based on chemical composition in not only the TIC, but in each of the EIPs as well, which indicates the utility of both the TIC and EIPs in association and discrimination determinations.

Once the neat diesel set had been analyzed, a series of spiking and burning experiments was performed on three common household matrices: cotton cloth, magazine, and carpet. A solvent extraction, consisting of agitation of the matrix in five mL of CS_2 for five minutes, was selected first based on a set of spike and recovery studies that demonstrated acceptable efficiency of the extraction. It was then determined that, although some unburned and burned matrices exhibit potential interference products, in the presence of a diesel, the interference peaks are masked by the components of the diesel itself. Finally, a set of spiked and burned diesels (two of which were treated as blind samples) was analyzed in an effort to simulate actual arson conditions. First, severe

spread was observed among replicate burnings in both the PPMC coefficients and scores plots from PCA, which confirms that the burning process is variable. Secondly, for PCA, it was determined that abundance plays a significant role when attempting to project scores for burned samples from eigenvectors calculated for a neat data set. In this case, a correction factor was applied to remedy the disparity in abundances between the neat and burned diesels. Ultimately, PPMC coefficients were a better marker for the identification of the blind samples, as differences in abundances did not affect the correlation coefficients. While it was possible to associate burned diesels to their neat counterparts using PCA, the association could only be made with minimal confidence. The PCA results for the EIP sets also showed promise for the association of burned samples to their neat counterparts. Overall, it is important to note that the diesels contained in the data sat are, by nature, very similar chemically. As a result, the ability to begin to make associations between neat and burned diesels, even at low confidence levels, is promising for the utility of the described methodology. It is likely that associations between burned samples and their neat counterparts can be made with higher confidence when the methodology is applied to a range of ignitable liquids that greatly differ in chemical composition.

5.2 Future Work

The future direction of this project lies mostly in the optimization of the already developed methodology. A few issues in both the analytical technique and the data pre-treatment and analysis phases must be addressed. It was concluded that a reproducible injection method is crucial to the precision of the technique, and consequently the accuracy of the results of the chemometric procedures. PCA is a procedure that focuses

on differences present in the chromatograms, which should be only due to actual differences in chemical composition. An imprecise injection method can introduce artificial variations in the data set, and thus lead to erroneous results. Although an effort was made to standardize a manual injection method, an investigation into a programmed injection method performed by an autosampler could improve precision and further reduce the chance for the introduction of artifacts.

The other obvious issue that needs to be addressed is the retention time alignment procedure. The current alignment algorithm is prone to misalignments, especially in the EIPs due to lower abundances as compared to the TIC. This particular peak-matching algorithm could be amended, with full optimization of all user-defined parameters, in order to be more appropriate for these specific diesel data sets. However, the fault in the alignment may be in the method with which the alignment itself is performed. More recent work published on retention time alignments suggests that piecewise alignment algorithms or warping algorithms may be more effective and less likely to result in misalignments than more basic peak-matching algorithms as was used in this research [41-44].

The last issue to be dealt with is the abundance problem in the scores projections for the burned diesel samples to be associated and discriminated. It was determined that significant disparities in the chromatographic abundance levels between the burned, extracted diesels and the neat diesels from which the eigenvectors were calculated can cause the scores for the burned data to be significantly different from the neat diesel scores. In this case, a correction factor was applied to the scores for the burned diesels based on average differences in abundance levels. However, no investigation was made

into the correction factor process, and in order for it to be a valid step, further study is required. Different or even multiple correction factors may be necessary in order to better represent the burned data, especially in actual arson cases when the abundances for the chromatograms collected from extracted fire debris will be so variable.

Once these aspects of the research are sufficiently remedied, more broad objectives can be addressed. Diesel was the ignitable liquid chosen for this study because of its complex chemical composition, but in reality diesel is rarely seen in arson cases. Typically, the lighter petroleum distillates like gasoline and lighter fluid are the more frequently encountered ignitable liquids. When applied to different classes of ignitable liquids, the methodology could prove more useful as an associative and discriminatory tool. Further investigation into matrix interferences is also essential before this methodology can be adapted into a forensic laboratory setting.

With further research, this methodology could be beneficial in the fire debris analysis section of a forensic laboratory. At the moment, ignitable liquid identifications are purely subjective in nature. The chemometric procedures offer a more objective approach for the determination of ignitable liquids. The methodology has the potential for complete automation, from the actual instrumental analysis all the way through the data analysis stage. Coupled with an extensive reference collection, this methodology could provide a powerful statistical method for the identification of ignitable liquid class, and potentially even the association of a burned ignitable liquid to its unburned counterpart.

APPENDICES

Appendix A

ASTM Classification Scheme

Table A.1 ASTM Ignitable Liquid Classification Scheme [4,5]

Class	Light (C_4-C_9)	Medium (C_8-C_{13})	Heavy (C_8-C_{20+})
Gasoline-all brands, including gasohol	Fresh gasoline is typically in the range of C_4-C_{12}		
Petroleum Distillates	Petroleum Ether Some Cigarette Lighter Fluids Some Camping Fuels	Some Charcoal Starters Some Paint Thinners Some Dry Cleaning Solvents	Kerosene Diesel Fuel Some Jet Fuels Some Charcoal Starters
Isoparaffinic Products	Aviation Gas Specialty Solvents	Some Charcoal Starters Some Paint Thinners Some Copier Toners	Some Commercial Specialty Solvents
Aromatic Products	Some Paint and Varnish Removers Some Automotive Parts Cleaners Xylenes, Toluene-based Products	Some Automotive Parts Cleaners Specialty Cleaning Solvents Some Insecticide Vehicles Fuel Additives	Some Insecticide Vehicles Industrial Cleaning Solvents
Naphthenic Paraffinic Products	Cyclohexane-based Solvents/Products	Some Charcoal Starters Some Insecticide Vehicles Lamp Oils	Some Insecticide Vehicles Lamp Oils Industrial Solvents
n-Alkanes Products	Solvents Pentane, Hexane, Heptane	Some Candle Oils Copier Toners	Some Candle Oils Carbonless Forms Copier Toners
De-Aromatized Distillates	Some Camping Fuels	Some Charcoal Starters Some Paint Thinners	Some Charcoal Starters Odorless Kerosene
Oxygenated Solvents	Alcohols, Ketones Some Lacquer Thinners Fuel Additives Surface Preparation Solvents	Some Lacquer Thinners Some Industrial Solvents Metal Cleaners/ Gloss Removers	
Others-Miscellaneous	Single Component Products Some Blended Products Some Enamel Reducers	Turpentine Products Some Blended Products Various Specialty Products	Some Blended Products Various Specialty Products

Table A.2 Chromatographic and Mass Spectral Characteristics of ASTM Ignitable Liquid Classes [4,5]

Class	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics
Gasoline-all brands, including gasohol	Present, less abundant than aromatics	Present, less abundant than aromatics	Abundant	Present
Petroleum Distillates	Abundant, Gaussian distribution	Present, less abundant than alkanes	Present, less abundant than alkanes	Present (depending on boiling range), less abundant than alkanes
Isoparaffinic Products	Branched alkanes abundant, n-alkanes absent or strongly diminished	Absent	Absent	Absent
Aromatic Products	Absent	Absent	Abundant	Abundant (depending on boiling range)
Naphthenic Paraffinic Products	Branched alkanes abundant, n-alkanes absent or strongly diminished	Abundant	Absent	Absent
n-Alkanes Products	Abundant	Absent	Absent	Absent
De-Aromatized Distillates	Abundant, Gaussian distribution	Present, less abundant than alkanes	Absent or strongly diminished	Absent or strongly diminished
Oxygenated Solvents	Composition may vary, presence of oxygenated organic compounds			

Appendix B

PPMC Coefficients for the TIC and EIPs of Ten Neat Diesels Analyzed in Triplicate

Table B.1 PPMC Coefficients for the TIC of Triplicate Analyses of Diesels 1-10

	D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
D1A	1.0000	0.9782	0.9782	0.9077	0.9240	0.9216	0.9480	0.9308	0.9378	0.9196	0.9295	0.9238	0.9201	0.9144	0.9129	0.8902	0.8974	0.8921	0.9448	0.9378	0.9563	0.9064	0.9009	0.8987	0.9074	0.9177	0.9044	0.9181	0.9300	0.9187
D1B	0.9782	1.0000	0.9864	0.9189	0.9138	0.9123	0.9464	0.9449	0.9474	0.9260	0.9258	0.9208	0.9200	0.9197	0.9197	0.8939	0.8933	0.8934	0.9493	0.9373	0.9539	0.9013	0.8975	0.8982	0.9115	0.9125	0.9074	0.9175	0.9139	0.9162
D1C	0.9782	0.9864	1.0000	0.9109	0.9103	0.9096	0.9514	0.9488	0.9441	0.9217	0.9236	0.9163	0.9198	0.9161	0.9210	0.8876	0.8958	0.8837	0.9354	0.9493	0.9509	0.8930	0.8892	0.8966	0.9065	0.9057	0.8915	0.9100	0.9093	0.9153
D2A	0.9077	0.9189	0.9109	1.0000	0.9895	0.9892	0.8895	0.8903	0.8958	0.9094	0.9055	0.9109	0.8841	0.8920	0.8881	0.8936	0.8915	0.8924	0.8709	0.8668	0.8835	0.8954	0.8965	0.8978	0.9127	0.9056	0.9036	0.9103	0.9017	0.9124
D2B	0.9240	0.9138	0.9103	0.9895	1.0000	0.9960	0.8961	0.8865	0.8957	0.9090	0.9108	0.9172	0.8898	0.8940	0.8893	0.8926	0.8941	0.8933	0.8755	0.8709	0.8926	0.8998	0.9004	0.8991	0.9122	0.9116	0.9071	0.9160	0.9147	0.9179
D2C	0.9216	0.9123	0.9096	0.9892	0.9960	1.0000	0.8947	0.8850	0.8925	0.9065	0.9082	0.9137	0.8874	0.8927	0.8881	0.8909	0.8917	0.8902	0.8764	0.8726	0.8896	0.8997	0.8971	0.8976	0.9104	0.9078	0.9064	0.9141	0.9132	0.9157
D3A	0.9480	0.9464	0.9514	0.8895	0.8961	0.8947	1.0000	0.9908	0.9930	0.9796	0.9828	0.9769	0.9708	0.9683	0.9703	0.9518	0.9589	0.9541	0.9742	0.9865	0.9900	0.9664	0.9662	0.9682	0.9653	0.9723	0.9600	0.9678	0.9653	0.9723
D3B	0.9308	0.9449	0.9488	0.8903	0.8865	0.8850	0.9908	1.0000	0.9936	0.9797	0.9771	0.9691	0.9652	0.9674	0.9694	0.9542	0.9568	0.9539	0.9739	0.9784	0.9836	0.9582	0.9606	0.9657	0.9652	0.9667	0.9593	0.9627	0.9520	0.9656
D3C	0.9378	0.9474	0.9441	0.8958	0.8957	0.8925	0.9930	0.9936	1.0000	0.9851	0.9841	0.9790	0.9709	0.9717	0.9726	0.9607	0.9629	0.9643	0.9800	0.9769	0.9897	0.9677	0.9721	0.9736	0.9717	0.9757	0.9680	0.9709	0.9626	0.9713
D4A	0.9196	0.9260	0.9217	0.9094	0.9090	0.9065	0.9796	0.9797	0.9851	1.0000	0.9954	0.9926	0.9645	0.9681	0.9677	0.9847	0.9844	0.9863	0.9601	0.9518	0.9708	0.9859	0.9886	0.9898	0.9891	0.9906	0.9837	0.9832	0.9759	0.9851
D4B	0.9295	0.9258	0.9236	0.9055	0.9108	0.9082	0.9828	0.9771	0.9841	0.9954	1.0000	0.9944	0.9674	0.9694	0.9677	0.9807	0.9844	0.9826	0.9636	0.9587	0.9747	0.9863	0.9892	0.9876	0.9869	0.9924	0.9847	0.9824	0.9799	0.9854
D4C	0.9238	0.9208	0.9163	0.9109	0.9172	0.9137	0.9769	0.9691	0.9790	0.9926	0.9944	1.0000	0.9702	0.9706	0.9670	0.9776	0.9807	0.9795	0.9542	0.9496	0.9684	0.9836	0.9888	0.9870	0.9889	0.9928	0.9858	0.9873	0.9854	0.9890
D5A	0.9201	0.9200	0.9198	0.8841	0.8898	0.8874	0.9708	0.9652	0.9709	0.9645	0.9674	0.9702	1.0000	0.9959	0.9920	0.9172	0.9236	0.9236	0.9552	0.9566	0.9704	0.9355	0.9395	0.9399	0.9728	0.9757	0.9702	0.9698	0.9679	0.9683
D5B	0.9144	0.9197	0.9161	0.8920	0.8940	0.8927	0.9683	0.9674	0.9717	0.9681	0.9694	0.9706	0.9959	1.0000	0.9932	0.9229	0.9256	0.9282	0.9590	0.9532	0.9674	0.9407	0.9428	0.9433	0.9792	0.9765	0.9767	0.9733	0.9685	0.9706
D5C	0.9129	0.9197	0.9210	0.8881	0.8893	0.8881	0.9703	0.9694	0.9726	0.9677	0.9677	0.9670	0.9920	0.9932	1.0000	0.9199	0.9252	0.9267	0.9501	0.9551	0.9666	0.9368	0.9391	0.9433	0.9721	0.9729	0.9696	0.9676	0.9605	0.9682
D6A	0.8902	0.8939	0.8876	0.8936	0.8926	0.8909	0.9518	0.9542	0.9607	0.9847	0.9807	0.9776	0.9172	0.9229	0.9199	1.0000	0.9947	0.9963	0.9367	0.9214	0.9399	0.9876	0.9912	0.9921	0.9696	0.9713	0.9655	0.9618	0.9535	0.9624
D6B	0.8974	0.8933	0.8958	0.8915	0.8941	0.8917	0.9589	0.9568	0.9629	0.9844	0.9844	0.9807	0.9236	0.9256	0.9252	0.9947	1.0000	0.9925	0.9346	0.9328	0.9436	0.9868	0.9917	0.9938	0.9684	0.9731	0.9635	0.9601	0.9568	0.9665
D6C	0.8921	0.8934	0.8837	0.8924	0.8933	0.8902	0.9541	0.9539	0.9643	0.9863	0.9826	0.9795	0.9236	0.9282	0.9267	0.9963	0.9925	1.0000	0.9380	0.9209	0.9446	0.9893	0.9933	0.9926	0.9713	0.9762	0.9688	0.9643	0.9576	0.9650
D7A	0.9448	0.9493	0.9354	0.8709	0.8755	0.8764	0.9742	0.9739	0.9800	0.9601	0.9636	0.9542	0.9552	0.9590	0.9501	0.9367	0.9346	0.9380	1.0000	0.9649	0.9817	0.9510	0.9462	0.9436	0.9536	0.9538	0.9594	0.9528	0.9503	0.9434
D7B	0.9378	0.9373	0.9493	0.8668	0.8709	0.8726	0.9865	0.9784	0.9769	0.9518	0.9587	0.9496	0.9566	0.9532	0.9551	0.9214	0.9328	0.9209	0.9649	1.0000	0.9746	0.9402	0.9366	0.9416	0.9390	0.9450	0.9340	0.9394	0.9405	0.9467
D7C	0.9563	0.9539	0.9509	0.8835	0.8926	0.8896	0.9900	0.9836	0.9897	0.9708	0.9747	0.9684	0.9704	0.9674	0.9666	0.9399	0.9436	0.9446	0.9817	0.9746	1.0000	0.9506	0.9558	0.9529	0.9566	0.9681	0.9568	0.9649	0.9603	0.9614
D8A	0.9064	0.9013	0.8930	0.8954	0.8998	0.8997	0.9664	0.9582	0.9677	0.9859	0.9863	0.9836	0.9355	0.9407	0.9368	0.9876	0.9868	0.9893	0.9510	0.9402	0.9506	1.0000	0.9928	0.9919	0.9773	0.9784	0.9747	0.9695	0.9710	0.9730
D8B	0.9009	0.8975	0.8892	0.8965	0.9004	0.8971	0.9662	0.9606	0.9721	0.9886	0.9892	0.9888	0.9395	0.9428	0.9391	0.9912	0.9917	0.9933	0.9462	0.9366	0.9558	0.9928	1.0000	0.9956	0.9778	0.9841	0.9760	0.9740	0.9693	0.9756
D8C	0.8987	0.8982	0.8966	0.8978	0.8991	0.8976	0.9682	0.9657	0.9736	0.9898	0.9876	0.9870	0.9399	0.9433	0.9433	0.9921	0.9938	0.9926	0.9436	0.9416	0.9529	0.9919	0.9956	1.0000	0.9787	0.9805	0.9728	0.9711	0.9665	0.9757
D9A	0.9074	0.9115	0.9065	0.9127	0.9122	0.9104	0.9653	0.9652	0.9717	0.9891	0.9869	0.9889	0.9728	0.9792	0.9721	0.9696	0.9684	0.9713	0.9536	0.9390	0.9566	0.9773	0.9778	0.9787	1.0000	0.9900	0.9884	0.9839	0.9800	0.9832
D9B	0.9177	0.9125	0.9057	0.9056	0.9116	0.9078	0.9723	0.9667	0.9757	0.9906	0.9924	0.9928	0.9757	0.9765	0.9729	0.9713	0.9731	0.9762	0.9538	0.9450	0.9681	0.9784	0.9841	0.9805	0.9900	1.0000	0.9891	0.9838	0.9807	0.9840
D9C	0.9044	0.9074	0.8915	0.9036	0.9071	0.9064	0.9600	0.9593	0.9680	0.9837	0.9847	0.9858	0.9702	0.9767	0.9696	0.9655	0.9635	0.9688	0.9594	0.9340	0.9568	0.9747	0.9760	0.9728	0.9884	0.9891	1.0000	0.9821	0.9770	0.9779
D10A	0.9181	0.9175	0.9100	0.9103	0.9160	0.9141	0.9678	0.9627	0.9709	0.9832	0.9824	0.9873	0.9698	0.9733	0.9676	0.9618	0.9601	0.9643	0.9528	0.9394	0.9649	0.9695	0.9740	0.9711	0.9839	0.9838	0.9821	1.0000	0.9896	0.9933
D10B	0.9300	0.9139	0.9093	0.9017	0.9147	0.9132	0.9653	0.9520	0.9626	0.9759	0.9799	0.9854	0.9679	0.9685	0.9605	0.9535	0.9568	0.9576	0.9503	0.9405	0.9603	0.9710	0.9693	0.9665	0.9800	0.9807	0.9770	0.9896	1.0000	0.9898
D10C	0.9187	0.9162	0.9153	0.9124	0.9179	0.9157	0.9723	0.9656	0.9713	0.9851	0.9854	0.9890	0.9683	0.9706	0.9682	0.9624	0.9665	0.9650	0.9434	0.9467	0.9614	0.9730	0.9756	0.9757	0.9832	0.9840	0.9779	0.9933	0.9898	1.0000

Table B.2 PPMC Coefficients for the Alkane EIP of Triplicate Analyses of Diesels 1-10

	D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
D1A	1.0000	0.9924	0.9906	0.9697	0.9755	0.9715	0.9486	0.9481	0.9493	0.9030	0.8986	0.9156	0.9233	0.9224	0.9211	0.9095	0.9180	0.9152	0.9514	0.9599	0.9119	0.9168	0.9019	0.9032	0.8994	0.9004	0.9054	0.8878	0.8987	0.8867
D1B	0.9924	1.0000	0.9803	0.9636	0.9669	0.9711	0.9444	0.9458	0.9484	0.9036	0.9005	0.9179	0.9154	0.9177	0.9208	0.9071	0.9147	0.9121	0.9519	0.9510	0.9253	0.9127	0.9041	0.8972	0.9089	0.9082	0.9058	0.8872	0.8969	0.8940
D1C	0.9906	0.9803	1.0000	0.9627	0.9667	0.9570	0.9322	0.9358	0.9358	0.8976	0.8924	0.9016	0.9205	0.9155	0.9072	0.8998	0.9076	0.9044	0.9383	0.9569	0.9050	0.9085	0.8940	0.8915	0.8765	0.8748	0.8922	0.8795	0.8913	0.8727
D2A	0.9697	0.9636	0.9627	1.0000	0.9938	0.9931	0.9726	0.9579	0.9689	0.9248	0.9363	0.9587	0.9618	0.9630	0.9593	0.9422	0.9576	0.9557	0.9479	0.9733	0.9269	0.9587	0.9495	0.9455	0.9408	0.9384	0.9586	0.9377	0.9538	0.9373
D2B	0.9755	0.9669	0.9667	0.9938	1.0000	0.9940	0.9745	0.9697	0.9729	0.9371	0.9382	0.9600	0.9665	0.9671	0.9647	0.9520	0.9588	0.9577	0.9545	0.9757	0.9195	0.9610	0.9490	0.9539	0.9430	0.9413	0.9548	0.9434	0.9470	0.9382
D2C	0.9715	0.9711	0.9570	0.9931	0.9940	1.0000	0.9763	0.9645	0.9732	0.9300	0.9433	0.9631	0.9584	0.9639	0.9641	0.9477	0.9588	0.9583	0.9576	0.9697	0.9316	0.9601	0.9499	0.9484	0.9504	0.9486	0.9565	0.9413	0.9480	0.9438
D3A	0.9486	0.9444	0.9322	0.9726	0.9745	0.9763	1.0000	0.9782	0.9937	0.9417	0.9509	0.9803	0.9708	0.9780	0.9823	0.9655	0.9802	0.9818	0.9706	0.9843	0.9414	0.9813	0.9711	0.9746	0.9692	0.9688	0.9784	0.9683	0.9723	0.9699
D3B	0.9481	0.9458	0.9358	0.9579	0.9697	0.9645	0.9782	1.0000	0.9874	0.9803	0.9483	0.9759	0.9742	0.9782	0.9773	0.9807	0.9732	0.9745	0.9626	0.9831	0.9409	0.9773	0.9738	0.9781	0.9697	0.9664	0.9669	0.9696	0.9471	0.9656
D3C	0.9493	0.9484	0.9358	0.9689	0.9729	0.9732	0.9937	0.9874	1.0000	0.9599	0.9568	0.9863	0.9780	0.9848	0.9835	0.9774	0.9847	0.9863	0.9763	0.9897	0.9531	0.9855	0.9809	0.9788	0.9755	0.9730	0.9809	0.9758	0.9720	0.9774
D4A	0.9030	0.9036	0.8976	0.9248	0.9371	0.9300	0.9417	0.9803	0.9599	1.0000	0.9299	0.9684	0.9646	0.9700	0.9584	0.9840	0.9640	0.9638	0.9362	0.9571	0.9383	0.9701	0.9744	0.9677	0.9640	0.9567	0.9572	0.9631	0.9335	0.9641
D4B	0.8986	0.9005	0.8924	0.9363	0.9382	0.9433	0.9509	0.9483	0.9568	0.9299	1.0000	0.9595	0.9541	0.9586	0.9549	0.9458	0.9496	0.9526	0.9146	0.9438	0.9018	0.9544	0.9521	0.9557	0.9460	0.9365	0.9512	0.9691	0.9431	0.9512
D4C	0.9156	0.9179	0.9016	0.9587	0.9600	0.9631	0.9803	0.9759	0.9863	0.9684	0.9595	1.0000	0.9813	0.9916	0.9880	0.9886	0.9931	0.9919	0.9577	0.9719	0.9492	0.9940	0.9942	0.9867	0.9918	0.9823	0.9922	0.9869	0.9823	0.9936
D5A	0.9233	0.9154	0.9205	0.9618	0.9665	0.9584	0.9708	0.9742	0.9780	0.9646	0.9541	0.9813	1.0000	0.9945	0.9853	0.9768	0.9803	0.9783	0.9409	0.9755	0.9203	0.9829	0.9808	0.9814	0.9673	0.9640	0.9826	0.9825	0.9761	0.9722
D5B	0.9224	0.9177	0.9155	0.9630	0.9671	0.9639	0.9780	0.9782	0.9848	0.9700	0.9586	0.9916	0.9945	1.0000	0.9910	0.9858	0.9881	0.9879	0.9558	0.9773	0.9377	0.9909	0.9882	0.9869	0.9802	0.9748	0.9888	0.9858	0.9792	0.9837
D5C	0.9211	0.9208	0.9072	0.9593	0.9647	0.9641	0.9823	0.9773	0.9835	0.9584	0.9549	0.9880	0.9853	0.9910	1.0000	0.9779	0.9836	0.9827	0.9530	0.9696	0.9310	0.9848	0.9802	0.9822	0.9812	0.9729	0.9860	0.9822	0.9740	0.9809
D6A	0.9095	0.9071	0.8998	0.9422	0.9520	0.9477	0.9655	0.9807	0.9774	0.9840	0.9458	0.9886	0.9768	0.9858	0.9779	1.0000	0.9891	0.9878	0.9516	0.9673	0.9389	0.9904	0.9912	0.9894	0.9810	0.9739	0.9770	0.9799	0.9638	0.9841
D6B	0.9180	0.9147	0.9076	0.9576	0.9588	0.9588	0.9802	0.9732	0.9847	0.9640	0.9496	0.9931	0.9803	0.9881	0.9836	0.9891	1.0000	0.9944	0.9568	0.9743	0.9389	0.9950	0.9901	0.9872	0.9800	0.9767	0.9889	0.9846	0.9780	0.9865
D6C	0.9152	0.9121	0.9044	0.9557	0.9577	0.9583	0.9818	0.9745	0.9863	0.9638	0.9526	0.9919	0.9783	0.9879	0.9827	0.9878	0.9944	1.0000	0.9568	0.9743	0.9389	0.9950	0.9901	0.9872	0.9800	0.9767	0.9889	0.9846	0.9780	0.9865
D7A	0.9514	0.9519	0.9383	0.9479	0.9545	0.9576	0.9706	0.9626	0.9763	0.9362	0.9146	0.9577	0.9409	0.9558	0.9530	0.9516	0.9568	0.9568	1.0000	0.9719	0.9659	0.9582	0.9478	0.9399	0.9485	0.9421	0.9450	0.9295	0.9360	0.9449
D7B	0.9599	0.9510	0.9569	0.9733	0.9757	0.9697	0.9843	0.9831	0.9897	0.9571	0.9438	0.9719	0.9755	0.9773	0.9696	0.9673	0.9744	0.9743	0.9719	1.0000	0.9544	0.9781	0.9716	0.9669	0.9544	0.9519	0.9692	0.9589	0.9618	0.9587
D7C	0.9119	0.9253	0.9050	0.9269	0.9195	0.9316	0.9414	0.9409	0.9531	0.9383	0.9018	0.9492	0.9203	0.9377	0.9310	0.9389	0.9426	0.9389	0.9659	0.9544	1.0000	0.9451	0.9511	0.9164	0.9454	0.9316	0.9387	0.9121	0.9217	0.9439
D8A	0.9168	0.9127	0.9085	0.9587	0.9610	0.9601	0.9813	0.9773	0.9855	0.9701	0.9544	0.9940	0.9829	0.9909	0.9848	0.9904	0.9954	0.9950	0.9582	0.9781	0.9451	1.0000	0.9941	0.9902	0.9827	0.9774	0.9903	0.9843	0.9798	0.9888
D8B	0.9019	0.9041	0.8940	0.9495	0.9490	0.9499	0.9711	0.9738	0.9809	0.9744	0.9521	0.9942	0.9808	0.9882	0.9802	0.9912	0.9930	0.9901	0.9478	0.9716	0.9511	0.9941	1.0000	0.9873	0.9852	0.9776	0.9890	0.9848	0.9800	0.9927
D8C	0.9032	0.8972	0.8915	0.9455	0.9539	0.9484	0.9746	0.9781	0.9788	0.9677	0.9557	0.9867	0.9814	0.9869	0.9822	0.9894	0.9880	0.9872	0.9399	0.9669	0.9164	0.9902	0.9873	1.0000	0.9779	0.9778	0.9807	0.9869	0.9721	0.9827
D9A	0.8994	0.9089	0.8765	0.9408	0.9430	0.9504	0.9692	0.9697	0.9755	0.9640	0.9460	0.9918	0.9673	0.9802	0.9812	0.9810	0.9810	0.9800	0.9485	0.9544	0.9454	0.9827	0.9852	0.9779	1.0000	0.9915	0.9863	0.9746	0.9640	0.9890
D9B	0.9004	0.9082	0.8748	0.9384	0.9413	0.9486	0.9688	0.9664	0.9730	0.9567	0.9365	0.9823	0.9640	0.9748	0.9729	0.9739	0.9753	0.9881	0.9450	0.9692	0.9387	0.9903	0.9890	0.9807	0.9863	0.9814	1.0000	0.9832	0.9833	0.9883
D9C	0.9054	0.9058	0.8922	0.9586	0.9548	0.9565	0.9784	0.9669	0.9809	0.9572	0.9512	0.9922	0.9826	0.9888	0.9860	0.9770	0.9881	0.9889	0.9450	0.9692	0.9387	0.9903	0.9890	0.9807	0.9863	0.9814	1.0000	0.9832	0.9833	0.9883
D10A	0.8878	0.8872	0.8795	0.9377	0.9434	0.9413	0.9683	0.9696	0.9758	0.9631	0.9691	0.9869	0.9825	0.9858	0.9822	0.9799	0.9820	0.9846	0.9295	0.9589	0.9121	0.9843	0.9848	0.9869	0.9746	0.9681	0.9832	1.0000	0.9774	0.9850
D10B	0.8987	0.8969	0.8913	0.9538	0.9470	0.9480	0.9723	0.9471	0.9720	0.9335	0.9431	0.9823	0.9761	0.9792	0.9740	0.9638	0.9835	0.9780	0.9360	0.9618	0.9217	0.9798	0.9800	0.9721	0.9640	0.9595	0.9833	0.9774	1.0000	0.9805
D10C	0.8867	0.8940	0.8727	0.9373	0.9382	0.9438	0.9699	0.9656	0.9774	0.9641	0.9512	0.9936	0.9722	0.9837	0.9809	0.9841	0.9876	0.9865	0.9449	0.9587	0.9439	0.9888	0.9927	0.9827	0.9890	0.9829	0.9883	0.9880	0.9805	1.0000

Table B.3 PPMC Coefficients for the Aromatic EIP of Triplicate Analyses of Diesels 1-10

	D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
D1A	1.0000	0.9376	0.9733	0.9488	0.9380	0.9479	0.8794	0.8752	0.8859	0.8823	0.8768	0.8895	0.8494	0.8506	0.8479	0.9142	0.8979	0.8989	0.8811	0.8779	0.8774	0.8823	0.8740	0.8746	0.8704	0.8669	0.8710	0.8926	0.8928	0.8960
D1B	0.9376	1.0000	0.9494	0.9048	0.9029	0.9053	0.8585	0.8414	0.8543	0.8640	0.8321	0.8577	0.8186	0.8255	0.8178	0.8766	0.8600	0.8693	0.8454	0.8326	0.8171	0.8585	0.8626	0.8614	0.8399	0.8249	0.8410	0.8386	0.8518	0.8522
D1C	0.9733	0.9494	1.0000	0.9418	0.9502	0.9533	0.8892	0.8880	0.8960	0.8939	0.8834	0.8931	0.8540	0.8556	0.8520	0.9090	0.9131	0.9112	0.8909	0.8831	0.8857	0.9002	0.8906	0.8928	0.8800	0.8703	0.8798	0.9040	0.9042	0.9053
D2A	0.9488	0.9048	0.9418	1.0000	0.9825	0.9842	0.8130	0.8106	0.8212	0.8075	0.8005	0.8142	0.7468	0.7496	0.7464	0.8604	0.8602	0.8581	0.8002	0.8076	0.8009	0.8226	0.8247	0.8244	0.7876	0.7803	0.7917	0.8291	0.8144	0.8346
D2B	0.9380	0.9029	0.9502	0.9825	1.0000	0.9912	0.8128	0.8172	0.8237	0.8082	0.7950	0.8105	0.7440	0.7514	0.7462	0.8552	0.8649	0.8544	0.8048	0.8094	0.8055	0.8323	0.8293	0.8267	0.7844	0.7815	0.7914	0.8385	0.8198	0.8388
D2C	0.9479	0.9053	0.9533	0.9842	0.9912	1.0000	0.8202	0.8182	0.8266	0.8153	0.8057	0.8178	0.7506	0.7563	0.7490	0.8643	0.8670	0.8614	0.8063	0.8146	0.8092	0.8366	0.8368	0.8297	0.7893	0.7813	0.7918	0.8408	0.8284	0.8415
D3A	0.8794	0.8585	0.8892	0.8130	0.8128	0.8202	1.0000	0.9771	0.9810	0.9823	0.9592	0.9774	0.9592	0.9639	0.9542	0.9607	0.9606	0.9529	0.9793	0.9817	0.9745	0.9689	0.9771	0.9744	0.9592	0.9575	0.9616	0.9511	0.9582	0.9662
D3B	0.8752	0.8414	0.8880	0.8106	0.8172	0.8182	0.9771	1.0000	0.9809	0.9692	0.9587	0.9682	0.9549	0.9602	0.9552	0.9469	0.9567	0.9447	0.9773	0.9732	0.9722	0.9762	0.9706	0.9664	0.9555	0.9496	0.9577	0.9556	0.9520	0.9653
D3C	0.8859	0.8543	0.8960	0.8212	0.8237	0.8266	0.9810	0.9809	1.0000	0.9745	0.9704	0.9791	0.9606	0.9615	0.9583	0.9622	0.9565	0.9651	0.9827	0.9824	0.9799	0.9709	0.9708	0.9727	0.9652	0.9545	0.9703	0.9662	0.9510	0.9591
D4A	0.8823	0.8640	0.8939	0.8075	0.8082	0.8153	0.9823	0.9692	0.9745	1.0000	0.9691	0.9905	0.9770	0.9793	0.9706	0.9650	0.9612	0.9556	0.9725	0.9688	0.9622	0.9782	0.9777	0.9787	0.9785	0.9760	0.9819	0.9535	0.9527	0.9621
D4B	0.8768	0.8321	0.8834	0.8005	0.7950	0.8057	0.9592	0.9587	0.9704	0.9691	1.0000	0.9806	0.9673	0.9635	0.9633	0.9531	0.9522	0.9584	0.9584	0.9637	0.9653	0.9591	0.9548	0.9508	0.9818	0.9585	0.9697	0.9542	0.9464	0.9465
D4C	0.8895	0.8577	0.8931	0.8142	0.8105	0.8178	0.9774	0.9682	0.9791	0.9905	0.9806	1.0000	0.9805	0.9790	0.9731	0.9689	0.9625	0.9625	0.9729	0.9707	0.9653	0.9761	0.9743	0.9750	0.9865	0.9782	0.9881	0.9597	0.9521	0.9597
D5A	0.8494	0.8186	0.8540	0.7468	0.7440	0.7506	0.9592	0.9549	0.9606	0.9770	0.9673	0.9805	1.0000	0.9921	0.9885	0.9253	0.9182	0.9170	0.9653	0.9573	0.9547	0.9486	0.9393	0.9438	0.9808	0.9750	0.9827	0.9255	0.9215	0.9243
D5B	0.8506	0.8255	0.8556	0.7496	0.7514	0.7563	0.9639	0.9602	0.9615	0.9793	0.9635	0.9790	0.9921	1.0000	0.9922	0.9259	0.9211	0.9158	0.9662	0.9577	0.9555	0.9560	0.9476	0.9459	0.9784	0.9760	0.9816	0.9257	0.9272	0.9328
D5C	0.8479	0.8178	0.8520	0.7464	0.7462	0.7490	0.9542	0.9552	0.9583	0.9706	0.9633	0.9731	0.9885	0.9922	1.0000	0.9222	0.9169	0.9149	0.9646	0.9556	0.9547	0.9479	0.9359	0.9372	0.9754	0.9702	0.9819	0.9266	0.9189	0.9270
D6A	0.9142	0.8766	0.9090	0.8604	0.8552	0.8643	0.9607	0.9469	0.9622	0.9650	0.9531	0.9689	0.9253	0.9259	0.9222	1.0000	0.9811	0.9844	0.9464	0.9568	0.9450	0.9668	0.9716	0.9727	0.9487	0.9384	0.9530	0.9638	0.9567	0.9680
D6B	0.8979	0.8600	0.9131	0.8602	0.8649	0.8670	0.9606	0.9567	0.9565	0.9612	0.9522	0.9625	0.9182	0.9211	0.9169	0.9811	1.0000	0.9799	0.9469	0.9523	0.9499	0.9723	0.9750	0.9744	0.9486	0.9379	0.9478	0.9659	0.9601	0.9767
D6C	0.8989	0.8693	0.9112	0.8581	0.8544	0.8614	0.9529	0.9447	0.9651	0.9556	0.9584	0.9625	0.9170	0.9158	0.9149	0.9844	0.9799	1.0000	0.9408	0.9533	0.9462	0.9620	0.9663	0.9682	0.9462	0.9270	0.9491	0.9641	0.9540	0.9601
D7A	0.8811	0.8454	0.8909	0.8002	0.8048	0.8063	0.9793	0.9773	0.9827	0.9725	0.9584	0.9729	0.9653	0.9662	0.9646	0.9464	0.9469	0.9408	1.0000	0.9812	0.9801	0.9680	0.9614	0.9602	0.9578	0.9574	0.9675	0.9617	0.9520	0.9587
D7B	0.8779	0.8326	0.8831	0.8076	0.8094	0.8146	0.9817	0.9732	0.9824	0.9688	0.9637	0.9707	0.9573	0.9577	0.9556	0.9568	0.9523	0.9533	0.9812	1.0000	0.9777	0.9613	0.9589	0.9539	0.9565	0.9440	0.9626	0.9576	0.9489	0.9577
D7C	0.8774	0.8171	0.8857	0.8009	0.8055	0.8092	0.9745	0.9722	0.9799	0.9622	0.9653	0.9653	0.9547	0.9555	0.9547	0.9450	0.9499	0.9462	0.9801	0.9777	1.0000	0.9555	0.9498	0.9546	0.9560	0.9558	0.9566	0.9606	0.9556	0.9580
D8A	0.8823	0.8585	0.9002	0.8226	0.8323	0.8366	0.9689	0.9762	0.9709	0.9782	0.9591	0.9761	0.9486	0.9560	0.9479	0.9668	0.9723	0.9620	0.9680	0.9613	0.9555	1.0000	0.9868	0.9794	0.9610	0.9556	0.9667	0.9682	0.9602	0.9713
D8B	0.8740	0.8626	0.8906	0.8247	0.8293	0.8368	0.9771	0.9706	0.9708	0.9777	0.9548	0.9743	0.9393	0.9476	0.9359	0.9716	0.9750	0.9663	0.9614	0.9589	0.9498	0.9868	1.0000	0.9866	0.9540	0.9486	0.9580	0.9584	0.9582	0.9696
D8C	0.8746	0.8614	0.8928	0.8244	0.8267	0.8297	0.9744	0.9664	0.9727	0.9787	0.9508	0.9750	0.9438	0.9459	0.9372	0.9727	0.9744	0.9682	0.9602	0.9539	0.9546	0.9794	0.9866	1.0000	0.9596	0.9606	0.9633	0.9579	0.9497	0.9664
D9A	0.8704	0.8399	0.8800	0.7876	0.7844	0.7893	0.9592	0.9555	0.9652	0.9785	0.9818	0.9865	0.9808	0.9784	0.9754	0.9487	0.9486	0.9462	0.9578	0.9565	0.9560	0.9610	0.9540	0.9596	1.0000	0.9739	0.9865	0.9406	0.9345	0.9421
D9B	0.8669	0.8249	0.8703	0.7803	0.7815	0.7813	0.9575	0.9496	0.9545	0.9760	0.9585	0.9782	0.9750	0.9760	0.9702	0.9384	0.9379	0.9270	0.9574	0.9440	0.9558	0.9556	0.9486	0.9606	0.9739	1.0000	0.9768	0.9374	0.9334	0.9426
D9C	0.8710	0.8410	0.8798	0.7917	0.7914	0.7918	0.9616	0.9577	0.9703	0.9819	0.9697	0.9881	0.9827	0.9816	0.9819	0.9530	0.9478	0.9491	0.9675	0.9626	0.9566	0.9667	0.9580	0.9633	0.9865	0.9768	1.0000	0.9493	0.9330	0.9435
D10A	0.8926	0.8386	0.9040	0.8291	0.8385	0.8408	0.9511	0.9556	0.9662	0.9535	0.9542	0.9597	0.9255	0.9257	0.9266	0.9638	0.9659	0.9641	0.9617	0.9576	0.9606	0.9682	0.9584	0.9579	0.9406	0.9374	0.9493	1.0000	0.9708	0.9763
D10B	0.8928	0.8518	0.9042	0.8144	0.8198	0.8284	0.9582	0.9520	0.9510	0.9527	0.9464	0.9521	0.9215	0.9272	0.9189	0.9567	0.9601	0.9540	0.9520	0.9489	0.9556	0.9602	0.9582	0.9497	0.9345	0.9334	0.9330	0.9708	1.0000	0.9819
D10C	0.8960	0.8522	0.9053	0.8346	0.8388	0.8415	0.9662	0.9653	0.9591	0.9621	0.9465	0.9597	0.9243	0.9328	0.9270	0.9680	0.9767	0.9601	0.9587	0.9577	0.9580	0.9713	0.9696	0.9664	0.9421	0.9426	0.9435	0.9763	0.9819	1.0000

Table B.4 PPMC Coefficients for the Indane EIP of Triplicate Analyses of Diesels 1-10

	D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
D1A	1.0000	0.9157	0.9327	0.8293	0.8382	0.7854	0.9309	0.9060	0.9256	0.9054	0.9074	0.9370	0.9205	0.9064	0.9259	0.9180	0.9200	0.9336	0.9304	0.9476	0.9201	0.9278	0.9057	0.9101	0.9220	0.9122	0.9041	0.9234	0.9188	0.9275
D1B	0.9157	1.0000	0.9731	0.9269	0.9406	0.8959	0.9446	0.9593	0.9579	0.9446	0.9596	0.9481	0.9321	0.9501	0.9355	0.9329	0.9330	0.9453	0.9051	0.9165	0.9002	0.9333	0.9320	0.9171	0.9052	0.9226	0.9152	0.9049	0.8882	0.9201
D1C	0.9327	0.9731	1.0000	0.9179	0.9217	0.8931	0.9440	0.9420	0.9489	0.9436	0.9513	0.9519	0.9310	0.9421	0.9466	0.9266	0.9317	0.9460	0.9012	0.9092	0.9143	0.9294	0.9089	0.9198	0.9023	0.9206	0.9115	0.8932	0.8870	0.9199
D2A	0.8293	0.9269	0.9179	1.0000	0.9758	0.9604	0.8756	0.8927	0.8901	0.9052	0.8973	0.8761	0.8686	0.8714	0.8648	0.8979	0.8894	0.8967	0.7960	0.8012	0.7997	0.8695	0.8427	0.8622	0.8311	0.8346	0.8420	0.8172	0.7884	0.7982
D2B	0.8382	0.9406	0.9217	0.9758	1.0000	0.9526	0.8738	0.8890	0.8891	0.8888	0.9026	0.8748	0.8582	0.8739	0.8595	0.8766	0.8625	0.8866	0.7912	0.8065	0.7956	0.8598	0.8567	0.8493	0.8384	0.8329	0.8337	0.8028	0.7911	0.7951
D2C	0.7854	0.8959	0.8931	0.9604	0.9526	1.0000	0.8204	0.8607	0.8663	0.8747	0.8815	0.8260	0.8321	0.8532	0.8425	0.8692	0.8431	0.8790	0.7594	0.7684	0.7915	0.8496	0.8188	0.8562	0.8265	0.8316	0.8442	0.7863	0.7782	0.7832
D3A	0.9309	0.9446	0.9440	0.8756	0.8738	0.8204	1.0000	0.9666	0.9680	0.9688	0.9640	0.9813	0.9795	0.9683	0.9733	0.9538	0.9518	0.9536	0.9402	0.9459	0.9333	0.9559	0.9250	0.9400	0.9370	0.9394	0.9263	0.9445	0.9276	0.9357
D3B	0.9060	0.9593	0.9420	0.8927	0.8890	0.8607	0.9666	1.0000	0.9752	0.9742	0.9853	0.9697	0.9693	0.9872	0.9730	0.9595	0.9535	0.9634	0.9465	0.9532	0.9345	0.9657	0.9608	0.9504	0.9370	0.9574	0.9600	0.9504	0.9142	0.9466
D3C	0.9256	0.9579	0.9489	0.8901	0.8891	0.8663	0.9680	0.9752	1.0000	0.9758	0.9776	0.9714	0.9837	0.9796	0.9750	0.9541	0.9473	0.9665	0.9432	0.9497	0.9411	0.9635	0.9358	0.9552	0.9578	0.9590	0.9513	0.9405	0.9441	0.9449
D4A	0.9054	0.9446	0.9436	0.9052	0.8888	0.8747	0.9688	0.9742	0.9758	1.0000	0.9801	0.9749	0.9804	0.9791	0.9804	0.9698	0.9643	0.9703	0.9281	0.9285	0.9365	0.9695	0.9249	0.9677	0.9529	0.9550	0.9511	0.9501	0.9340	0.9350
D4B	0.9074	0.9596	0.9513	0.8973	0.9026	0.8815	0.9640	0.9853	0.9776	0.9801	1.0000	0.9744	0.9734	0.9911	0.9799	0.9570	0.9449	0.9690	0.9375	0.9433	0.9324	0.9667	0.9591	0.9549	0.9504	0.9601	0.9657	0.9425	0.9263	0.9481
D4C	0.9370	0.9481	0.9519	0.8761	0.8748	0.8260	0.9813	0.9697	0.9714	0.9749	0.9744	1.0000	0.9738	0.9738	0.9755	0.9468	0.9494	0.9545	0.9395	0.9443	0.9258	0.9534	0.9352	0.9383	0.9330	0.9435	0.9356	0.9380	0.9235	0.9444
D5A	0.9205	0.9321	0.9310	0.8686	0.8582	0.8321	0.9795	0.9693	0.9837	0.9804	0.9734	0.9738	1.0000	0.9821	0.9853	0.9590	0.9481	0.9621	0.9475	0.9505	0.9451	0.9674	0.9249	0.9586	0.9650	0.9579	0.9518	0.9556	0.9528	0.9443
D5B	0.9064	0.9501	0.9421	0.8714	0.8739	0.8532	0.9683	0.9872	0.9796	0.9791	0.9911	0.9738	0.9821	1.0000	0.9857	0.9566	0.9444	0.9653	0.9501	0.9561	0.9478	0.9708	0.9552	0.9600	0.9574	0.9699	0.9704	0.9536	0.9375	0.9571
D5C	0.9259	0.9355	0.9466	0.8648	0.8595	0.8425	0.9733	0.9730	0.9750	0.9804	0.9799	0.9755	0.9853	0.9857	1.0000	0.9555	0.9492	0.9636	0.9465	0.9513	0.9498	0.9664	0.9310	0.9604	0.9580	0.9586	0.9597	0.9540	0.9377	0.9511
D6A	0.9180	0.9329	0.9266	0.8979	0.8766	0.8692	0.9538	0.9595	0.9541	0.9698	0.9570	0.9468	0.9590	0.9566	0.9555	1.0000	0.9843	0.9870	0.9427	0.9452	0.9534	0.9885	0.9357	0.9807	0.9590	0.9674	0.9602	0.9737	0.9454	0.9496
D6B	0.9200	0.9330	0.9317	0.8894	0.8625	0.8431	0.9518	0.9535	0.9473	0.9643	0.9449	0.9494	0.9481	0.9444	0.9492	0.9843	1.0000	0.9767	0.9460	0.9418	0.9507	0.9769	0.9302	0.9715	0.9427	0.9587	0.9456	0.9599	0.9289	0.9487
D6C	0.9336	0.9453	0.9460	0.8967	0.8866	0.8790	0.9536	0.9634	0.9665	0.9703	0.9690	0.9545	0.9621	0.9653	0.9636	0.9870	0.9767	1.0000	0.9507	0.9590	0.9650	0.9907	0.9533	0.9827	0.9693	0.9766	0.9729	0.9643	0.9555	0.9632
D7A	0.9304	0.9051	0.9012	0.7960	0.7912	0.7594	0.9402	0.9465	0.9432	0.9281	0.9375	0.9395	0.9475	0.9501	0.9465	0.9427	0.9460	0.9507	1.0000	0.9839	0.9670	0.9659	0.9590	0.9504	0.9502	0.9669	0.9647	0.9578	0.9470	0.9732
D7B	0.9476	0.9165	0.9092	0.8012	0.8065	0.7684	0.9459	0.9532	0.9497	0.9285	0.9433	0.9443	0.9505	0.9561	0.9513	0.9452	0.9418	0.9590	0.9839	1.0000	0.9702	0.9694	0.9627	0.9481	0.9551	0.9674	0.9654	0.9639	0.9501	0.9755
D7C	0.9201	0.9002	0.9143	0.7997	0.7956	0.7915	0.9333	0.9345	0.9411	0.9365	0.9324	0.9258	0.9451	0.9478	0.9498	0.9534	0.9507	0.9650	0.9670	0.9702	1.0000	0.9750	0.9291	0.9747	0.9672	0.9810	0.9629	0.9588	0.9645	0.9701
D8A	0.9278	0.9333	0.9294	0.8695	0.8598	0.8496	0.9559	0.9657	0.9635	0.9695	0.9667	0.9534	0.9674	0.9708	0.9664	0.9885	0.9769	0.9907	0.9659	0.9694	0.9750	1.0000	0.9572	0.9881	0.9771	0.9863	0.9802	0.9778	0.9661	0.9728
D8B	0.9057	0.9320	0.9089	0.8427	0.8567	0.8188	0.9250	0.9608	0.9358	0.9249	0.9591	0.9352	0.9249	0.9552	0.9310	0.9357	0.9302	0.9533	0.9590	0.9627	0.9291	0.9572	1.0000	0.9338	0.9321	0.9545	0.9689	0.9305	0.9109	0.9555
D8C	0.9101	0.9171	0.9198	0.8622	0.8493	0.8562	0.9400	0.9504	0.9552	0.9677	0.9549	0.9383	0.9586	0.9600	0.9604	0.9807	0.9715	0.9827	0.9504	0.9481	0.9747	0.9881	0.9338	1.0000	0.9808	0.9834	0.9706	0.9663	0.9658	0.9577
D9A	0.9220	0.9052	0.9023	0.8311	0.8384	0.8265	0.9370	0.9370	0.9578	0.9529	0.9504	0.9330	0.9650	0.9574	0.9580	0.9590	0.9427	0.9693	0.9502	0.9551	0.9672	0.9771	0.9321	0.9808	1.0000	0.9777	0.9658	0.9583	0.9814	0.9505
D9B	0.9122	0.9226	0.9206	0.8346	0.8329	0.8316	0.9394	0.9574	0.9590	0.9550	0.9601	0.9435	0.9579	0.9699	0.9586	0.9674	0.9587	0.9766	0.9669	0.9674	0.9810	0.9863	0.9545	0.9834	0.9777	1.0000	0.9830	0.9640	0.9692	0.9782
D9C	0.9041	0.9152	0.9115	0.8420	0.8337	0.8442	0.9263	0.9600	0.9513	0.9511	0.9657	0.9356	0.9518	0.9704	0.9597	0.9602	0.9456	0.9729	0.9647	0.9654	0.9629	0.9802	0.9689	0.9706	0.9658	0.9830	1.0000	0.9579	0.9475	0.9722
D10A	0.9234	0.9049	0.8932	0.8172	0.8028	0.7863	0.9445	0.9504	0.9405	0.9501	0.9425	0.9380	0.9556	0.9536	0.9540	0.9737	0.9599	0.9643	0.9578	0.9639	0.9588	0.9778	0.9305	0.9663	0.9583	0.9640	0.9579	1.0000	0.9626	0.9676
D10B	0.9188	0.8882	0.8870	0.7884	0.7911	0.7782	0.9276	0.9142	0.9441	0.9340	0.9263	0.9235	0.9528	0.9375	0.9377	0.9454	0.9289	0.9555	0.9470	0.9501	0.9645	0.9661	0.9109	0.9658	0.9814	0.9692	0.9475	0.9626	1.0000	0.9625
D10C	0.9275	0.9201	0.9199	0.7982	0.7951	0.7832	0.9357	0.9466	0.9449	0.9350	0.9481	0.9444	0.9443	0.9571	0.9511	0.9496	0.9487	0.9632	0.9732	0.9755	0.9701	0.9728	0.9555	0.9577	0.9505	0.9782	0.9722	0.9676	0.9625	1.0000

Table B.5 PPMC Coefficients for the OCP EIP of Triplicate Analyses of Diesels 1-10

D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
1.0000	0.9561	0.9651	0.9055	0.9020	0.9009	0.9046	0.9123	0.9013	0.8670	0.8671	0.8649	0.8731	0.8693	0.8512	0.8574	0.8656	0.8768	0.9507	0.9368	0.9446	0.8720	0.8472	0.8501	0.8659	0.8572	0.8424	0.8587	0.8944	0.8544
0.9561	1.0000	0.9719	0.9140	0.9078	0.9288	0.9248	0.9242	0.9146	0.8850	0.8827	0.8494	0.8658	0.8771	0.8811	0.8637	0.8452	0.8485	0.9279	0.9138	0.9356	0.8783	0.8380	0.8553	0.8680	0.8750	0.8580	0.8598	0.8689	0.8672
0.9651	0.9719	1.0000	0.9132	0.9344	0.9269	0.9241	0.9112	0.9092	0.8941	0.8963	0.8710	0.8691	0.8822	0.8709	0.8526	0.8622	0.8583	0.9399	0.8976	0.9240	0.8714	0.8669	0.8743	0.8667	0.8744	0.8625	0.8681	0.8819	0.8472
0.9055	0.9140	0.9132	1.0000	0.9627	0.9662	0.9427	0.9279	0.9251	0.9335	0.9282	0.9339	0.9375	0.9255	0.9220	0.9193	0.8857	0.8928	0.9056	0.9072	0.9286	0.9258	0.8849	0.8865	0.9334	0.9140	0.9014	0.9303	0.9351	0.9168
0.9020	0.9078	0.9344	0.9627	1.0000	0.9660	0.9352	0.9096	0.9170	0.9361	0.9441	0.9356	0.9133	0.9257	0.9147	0.9061	0.9079	0.9060	0.9144	0.8784	0.9093	0.9121	0.9086	0.9185	0.9283	0.9189	0.9106	0.9295	0.9376	0.9022
0.9009	0.9288	0.9269	0.9662	0.9660	1.0000	0.9443	0.9407	0.9413	0.9439	0.9402	0.9217	0.9160	0.9373	0.9282	0.9156	0.9079	0.9089	0.9189	0.8979	0.9207	0.9217	0.9200	0.9144	0.9336	0.9319	0.9356	0.9342	0.9259	0.9230
0.9046	0.9248	0.9241	0.9427	0.9352	0.9443	1.0000	0.9686	0.9515	0.9516	0.9555	0.9335	0.9325	0.9520	0.9473	0.9336	0.9096	0.9035	0.9384	0.9405	0.9454	0.9188	0.9206	0.9247	0.9391	0.9246	0.9210	0.9315	0.9295	0.9317
0.9123	0.9242	0.9112	0.9279	0.9096	0.9407	0.9686	1.0000	0.9736	0.9437	0.9439	0.9308	0.9309	0.9504	0.9254	0.9125	0.9143	0.9156	0.9499	0.9472	0.9525	0.9266	0.9284	0.9174	0.9271	0.9263	0.9154	0.9216	0.9243	0.9295
0.9013	0.9146	0.9092	0.9251	0.9170	0.9413	0.9515	0.9736	1.0000	0.9504	0.9556	0.9308	0.9378	0.9491	0.9314	0.9129	0.9245	0.9285	0.9468	0.9346	0.9456	0.9396	0.9288	0.9190	0.9432	0.9449	0.9343	0.9346	0.9299	0.9192
0.8670	0.8850	0.8941	0.9335	0.9361	0.9439	0.9516	0.9437	0.9504	1.0000	0.9727	0.9703	0.9412	0.9596	0.9505	0.9287	0.9303	0.9360	0.9232	0.8976	0.9141	0.9516	0.9452	0.9429	0.9564	0.9489	0.9522	0.9548	0.9494	0.9281
0.8671	0.8827	0.8963	0.9282	0.9441	0.9402	0.9555	0.9439	0.9556	0.9727	1.0000	0.9667	0.9390	0.9610	0.9431	0.9316	0.9524	0.9423	0.9163	0.8976	0.9086	0.9287	0.9421	0.9495	0.9633	0.9539	0.9492	0.9545	0.9525	0.9282
0.8649	0.8494	0.8710	0.9339	0.9356	0.9217	0.9335	0.9308	0.9308	0.9703	0.9667	1.0000	0.9495	0.9536	0.9272	0.9171	0.9360	0.9432	0.9057	0.8939	0.9021	0.9328	0.9289	0.9340	0.9513	0.9325	0.9266	0.9536	0.9656	0.9227
0.8731	0.8658	0.8691	0.9375	0.9133	0.9160	0.9325	0.9309	0.9378	0.9412	0.9390	0.9495	1.0000	0.9742	0.9631	0.8943	0.8899	0.8972	0.9217	0.9219	0.9344	0.9205	0.8913	0.8865	0.9564	0.9401	0.9257	0.9453	0.9540	0.9263
0.8693	0.8771	0.8822	0.9255	0.9257	0.9373	0.9520	0.9504	0.9491	0.9596	0.9610	0.9536	0.9742	1.0000	0.9761	0.9082	0.9129	0.9136	0.9305	0.9150	0.9253	0.9211	0.9298	0.9256	0.9635	0.9528	0.9549	0.9530	0.9535	0.9433
0.8512	0.8811	0.8709	0.9220	0.9147	0.9282	0.9473	0.9254	0.9314	0.9505	0.9431	0.9272	0.9631	0.9761	1.0000	0.9069	0.8830	0.8848	0.9141	0.9059	0.9172	0.9081	0.8925	0.9044	0.9581	0.9475	0.9494	0.9409	0.9307	0.9355
0.8574	0.8637	0.8526	0.9193	0.9061	0.9156	0.9336	0.9125	0.9129	0.9287	0.9316	0.9171	0.8943	0.9082	0.9069	1.0000	0.9284	0.9492	0.8868	0.8980	0.9066	0.9316	0.9203	0.9208	0.9454	0.9208	0.9251	0.9281	0.9361	0.9491
0.8656	0.8452	0.8622	0.8857	0.9079	0.9079	0.9096	0.9143	0.9245	0.9303	0.9524	0.9360	0.8899	0.9129	0.8830	0.9284	1.0000	0.9742	0.9042	0.8970	0.8900	0.9122	0.9515	0.9630	0.9333	0.9308	0.9336	0.9301	0.9395	0.9124
0.8768	0.8485	0.8583	0.8928	0.9060	0.9089	0.9035	0.9156	0.9285	0.9360	0.9423	0.9432	0.8972	0.9136	0.8848	0.9492	0.9742	1.0000	0.9135	0.9064	0.9036	0.9370	0.9498	0.9574	0.9435	0.9348	0.9348	0.9321	0.9478	0.9200
0.9507	0.9279	0.9399	0.9056	0.9144	0.9189	0.9384	0.9499	0.9468	0.9232	0.9163	0.9057	0.9217	0.9305	0.9141	0.8868	0.9042	0.9135	1.0000	0.9560	0.9712	0.9167	0.9144	0.9135	0.9183	0.9250	0.9175	0.9151	0.9268	0.8978
0.9368	0.9138	0.8976	0.9072	0.8784	0.8979	0.9405	0.9472	0.9346	0.8976	0.8976	0.8939	0.9219	0.9150	0.9059	0.8980	0.8970	0.9064	0.9560	1.0000	0.9764	0.9030	0.8750	0.8838	0.9120	0.9031	0.8870	0.8985	0.9167	0.9056
0.9446	0.9356	0.9240	0.9286	0.9093	0.9207	0.9454	0.9525	0.9456	0.9141	0.9086	0.9021	0.9344	0.9253	0.9172	0.9066	0.8900	0.9036	0.9712	0.9764	1.0000	0.9343	0.8890	0.8944	0.9242	0.9235	0.9033	0.9201	0.9342	0.9196
0.8720	0.8783	0.8714	0.9258	0.9121	0.9217	0.9188	0.9266	0.9396	0.9516	0.9287	0.9328	0.9205	0.9211	0.9081	0.9316	0.9122	0.9370	0.9167	0.9030	0.9343	1.0000	0.9279	0.9271	0.9534	0.9483	0.9328	0.9479	0.9469	0.9307
0.8472	0.8380	0.8669	0.8849	0.9086	0.9200	0.9206	0.9284	0.9288	0.9452	0.9421	0.9289	0.8913	0.9298	0.8925	0.9203	0.9515	0.9498	0.9144	0.8750	0.8890	0.9279	1.0000	0.9683	0.9350	0.9336	0.9482	0.9394	0.9317	0.9282
0.8501	0.8553	0.8743	0.8865	0.9185	0.9144	0.9247	0.9174	0.9190	0.9429	0.9495	0.9340	0.8865	0.9256	0.9044	0.9208	0.9630	0.9524	0.9135	0.8838	0.8944	0.9271	0.9683	1.0000	0.9375	0.9480	0.9502	0.9413	0.9337	0.9177
0.8659	0.8680	0.8667	0.9334	0.9283	0.9336	0.9391	0.9271	0.9432	0.9564	0.9633	0.9513	0.9564	0.9635	0.9581	0.9454	0.9333	0.9435	0.9183	0.9120	0.9242	0.9534	0.9350	0.9375	1.0000	0.9739	0.9684	0.9743	0.9679	0.9564
0.8572	0.8750	0.8744	0.9140	0.9189	0.9319	0.9246	0.9263	0.9449	0.9489	0.9539	0.9325	0.9401	0.9528	0.9475	0.9208	0.9308	0.9348	0.9250	0.9031	0.9235	0.9483	0.9336	0.9480	0.9739	1.0000	0.9750	0.9673	0.9509	0.9292
0.8424	0.8580	0.8625	0.9014	0.9106	0.9356	0.9210	0.9154	0.9343	0.9522	0.9492	0.9266	0.9257	0.9549	0.9494	0.9251	0.9336	0.9348	0.9175	0.8870	0.9033	0.9328	0.9482	0.9502	0.9684	0.9750	1.0000	0.9657	0.9449	0.9390
0.8587	0.8598	0.8681	0.9303	0.9295	0.9342	0.9315	0.9216	0.9346	0.9548	0.9545	0.9536	0.9453	0.9530	0.9409	0.9281	0.9301	0.9321	0.9151	0.8985	0.9201	0.9479	0.9394	0.9413	0.9743	0.9673	0.9657	1.0000	0.9778	0.9567
0.8944	0.8689	0.8819	0.9351	0.9376	0.9259	0.9295	0.9243	0.9299	0.9494	0.9525	0.9656	0.9540	0.9535	0.9307	0.9361	0.9395	0.9478	0.9268	0.9167	0.9342	0.9469	0.9317	0.9337	0.9679	0.9509	0.9449	0.9778	1.0000	0.9564
0.8544	0.8672	0.8472	0.9168	0.9022	0.9230	0.9317	0.9295	0.9192	0.9281	0.9282	0.9227	0.9263	0.9433	0.9355	0.9491	0.9124	0.9200	0.8978	0.9056	0.9196	0.9307	0.9282	0.9177	0.9564	0.9292	0.9390	0.9567	0.9564	1.0000

Table B.6 PPMC Coefficients for the PNA EIP of Triplicate Analyses of Diesels 1-10

	D1A	D1B	D1C	D2A	D2B	D2C	D3A	D3B	D3C	D4A	D4B	D4C	D5A	D5B	D5C	D6A	D6B	D6C	D7A	D7B	D7C	D8A	D8B	D8C	D9A	D9B	D9C	D10A	D10B	D10C
D1A	1.0000	0.9772	0.9774	0.8566	0.8948	0.8788	0.8514	0.8758	0.8497	0.8201	0.8215	0.8193	0.7997	0.8282	0.7918	0.7825	0.7959	0.7931	0.8784	0.8630	0.8645	0.8032	0.8140	0.8130	0.7822	0.7944	0.7662	0.8461	0.8188	0.8308
D1B	0.9772	1.0000	0.9840	0.8720	0.8652	0.8857	0.8794	0.8869	0.8591	0.8110	0.8293	0.8182	0.8287	0.8390	0.7775	0.7918	0.7981	0.7940	0.8852	0.8979	0.8892	0.8165	0.8195	0.8159	0.7866	0.7958	0.7837	0.8560	0.8441	0.8491
D1C	0.9774	0.9840	1.0000	0.8707	0.8649	0.8803	0.8852	0.8929	0.8627	0.8169	0.8340	0.8216	0.8368	0.8438	0.7784	0.8019	0.8037	0.7997	0.8910	0.8975	0.8934	0.8233	0.8249	0.8172	0.7952	0.7974	0.7915	0.8617	0.8436	0.8520
D2A	0.8566	0.8720	0.8707	1.0000	0.8662	0.9450	0.8367	0.8122	0.7996	0.7575	0.8085	0.7801	0.8423	0.8034	0.6675	0.8367	0.7938	0.7989	0.8022	0.8365	0.8478	0.8477	0.8175	0.7936	0.8055	0.7667	0.8346	0.8140	0.8277	0.8447
D2B	0.8948	0.8652	0.8649	0.8662	1.0000	0.9120	0.7785	0.8355	0.8071	0.8600	0.8349	0.8521	0.7434	0.8170	0.8399	0.7992	0.8378	0.8337	0.8000	0.7759	0.7736	0.7946	0.8355	0.8440	0.7923	0.8439	0.7594	0.8307	0.7771	0.8045
D2C	0.8788	0.8857	0.8803	0.9450	0.9120	1.0000	0.8595	0.8425	0.8057	0.8090	0.8447	0.8223	0.8346	0.8262	0.7382	0.8357	0.8304	0.8237	0.8050	0.8550	0.8335	0.8449	0.8401	0.8295	0.8138	0.8204	0.8128	0.8449	0.8508	0.8483
D3A	0.8514	0.8794	0.8852	0.8367	0.7785	0.8595	1.0000	0.9660	0.9323	0.9051	0.9497	0.9238	0.9623	0.9505	0.8394	0.9381	0.9286	0.9255	0.9355	0.9815	0.9586	0.9533	0.9405	0.9332	0.9131	0.9128	0.9246	0.9617	0.9621	0.9618
D3B	0.8758	0.8869	0.8929	0.8122	0.8355	0.8425	0.9660	1.0000	0.9445	0.9598	0.9699	0.9602	0.9360	0.9689	0.9095	0.9467	0.9592	0.9502	0.9521	0.9597	0.9413	0.9500	0.9569	0.9597	0.9300	0.9519	0.9128	0.9815	0.9592	0.9642
D3C	0.8497	0.8591	0.8627	0.7996	0.8071	0.8057	0.9323	0.9445	1.0000	0.9192	0.9292	0.9374	0.9355	0.9585	0.8909	0.9309	0.9157	0.9498	0.9515	0.9280	0.9578	0.9452	0.9636	0.9514	0.9400	0.9058	0.9477	0.9331	0.9088	0.9574
D4A	0.8201	0.8110	0.8169	0.7575	0.8600	0.8090	0.9051	0.9598	0.9192	1.0000	0.9749	0.9840	0.8903	0.9640	0.9595	0.9403	0.9808	0.9712	0.9168	0.8863	0.8689	0.9302	0.9592	0.9729	0.9351	0.9788	0.8953	0.9714	0.9299	0.9371
D4B	0.8215	0.8293	0.8340	0.8085	0.8349	0.8447	0.9497	0.9699	0.9292	0.9749	1.0000	0.9871	0.9397	0.9802	0.9251	0.9635	0.9894	0.9789	0.9182	0.9325	0.9089	0.9593	0.9750	0.9830	0.9407	0.9826	0.9309	0.9877	0.9639	0.9681
D4C	0.8193	0.8182	0.8216	0.7801	0.8521	0.8223	0.9238	0.9602	0.9374	0.9840	0.9871	1.0000	0.9130	0.9780	0.9577	0.9474	0.9860	0.9829	0.9146	0.9080	0.8930	0.9426	0.9759	0.9896	0.9348	0.9861	0.9193	0.9773	0.9383	0.9546
D5A	0.7997	0.8287	0.8368	0.8423	0.7434	0.8346	0.9623	0.9360	0.9355	0.8903	0.9397	0.9130	1.0000	0.9592	0.8163	0.9596	0.9188	0.9316	0.9217	0.9467	0.9567	0.9710	0.9443	0.9225	0.9563	0.9025	0.9739	0.9435	0.9567	0.9711
D5B	0.8282	0.8390	0.8438	0.8034	0.8170	0.8262	0.9505	0.9689	0.9585	0.9640	0.9802	0.9780	0.9592	1.0000	0.9231	0.9646	0.9695	0.9773	0.9404	0.9374	0.9372	0.9648	0.9780	0.9773	0.9610	0.9696	0.9572	0.9789	0.9584	0.9781
D5C	0.7918	0.7775	0.7784	0.6675	0.8399	0.7382	0.8394	0.9095	0.8909	0.9595	0.9251	0.9577	0.8163	0.9231	1.0000	0.8504	0.9241	0.9194	0.8647	0.8347	0.8165	0.8429	0.9093	0.9378	0.8615	0.9513	0.8237	0.9164	0.8581	0.8743
D6A	0.7825	0.7918	0.8019	0.8367	0.7992	0.8357	0.9381	0.9467	0.9309	0.9403	0.9635	0.9474	0.9596	0.9646	0.8504	1.0000	0.9662	0.9743	0.9199	0.9134	0.9238	0.9882	0.9720	0.9585	0.9747	0.9409	0.9722	0.9619	0.9534	0.9752
D6B	0.7959	0.7981	0.8037	0.7938	0.8378	0.8304	0.9286	0.9592	0.9157	0.9808	0.9894	0.9860	0.9188	0.9695	0.9241	0.9662	1.0000	0.9843	0.9080	0.9066	0.8824	0.9565	0.9724	0.9833	0.9402	0.9825	0.9225	0.9815	0.9508	0.9565
D6C	0.7931	0.7940	0.7997	0.7989	0.8337	0.8237	0.9255	0.9502	0.9498	0.9712	0.9789	0.9829	0.9316	0.9773	0.9194	0.9743	0.9843	1.0000	0.9193	0.9051	0.9058	0.9696	0.9890	0.9896	0.9611	0.9706	0.9535	0.9695	0.9386	0.9682
D7A	0.8784	0.8852	0.8910	0.8022	0.8000	0.8050	0.9355	0.9521	0.9515	0.9168	0.9182	0.9146	0.9217	0.9404	0.8647	0.9199	0.9080	0.9193	1.0000	0.9244	0.9396	0.9330	0.9222	0.9155	0.9258	0.8868	0.9165	0.9367	0.9201	0.9352
D7B	0.8630	0.8979	0.8975	0.8365	0.7759	0.8550	0.9815	0.9597	0.9280	0.8863	0.9325	0.9080	0.9467	0.9374	0.8347	0.9134	0.9066	0.9051	0.9244	1.0000	0.9603	0.9309	0.9267	0.9204	0.8876	0.9009	0.9036	0.9490	0.9535	0.9556
D7C	0.8645	0.8892	0.8934	0.8478	0.7736	0.8335	0.9586	0.9413	0.9578	0.8689	0.9089	0.8930	0.9567	0.9372	0.8165	0.9238	0.8824	0.9058	0.9396	0.9603	1.0000	0.9434	0.9327	0.9114	0.9175	0.8727	0.9407	0.9227	0.9212	0.9551
D8A	0.8032	0.8165	0.8233	0.8477	0.7946	0.8449	0.9533	0.9500	0.9452	0.9302	0.9593	0.9426	0.9710	0.9648	0.8429	0.9882	0.9565	0.9696	0.9330	0.9309	0.9434	1.0000	0.9742	0.9571	0.9772	0.9296	0.9774	0.9612	0.9560	0.9797
D8B	0.8140	0.8195	0.8249	0.8175	0.8355	0.8401	0.9405	0.9569	0.9636	0.9592	0.9750	0.9759	0.9443	0.9780	0.9093	0.9720	0.9724	0.9890	0.9222	0.9267	0.9327	0.9742	1.0000	0.9884	0.9626	0.9629	0.9590	0.9682	0.9420	0.9768
D8C	0.8130	0.8159	0.8172	0.7936	0.8440	0.8295	0.9332	0.9597	0.9514	0.9729	0.9830	0.9896	0.9225	0.9773	0.9378	0.9585	0.9833	0.9896	0.9155	0.9204	0.9114	0.9571	0.9884	1.0000	0.9411	0.9793	0.9351	0.9746	0.9398	0.9665
D9A	0.7822	0.7866	0.7952	0.8055	0.7923	0.8138	0.9131	0.9300	0.9400	0.9351	0.9407	0.9348	0.9563	0.9610	0.8615	0.9747	0.9402	0.9611	0.9258	0.8876	0.9175	0.9772	0.9626	0.9411	1.0000	0.9230	0.9735	0.9400	0.9315	0.9594
D9B	0.7944	0.7958	0.7974	0.7667	0.8439	0.8204	0.9128	0.9519	0.9058	0.9788	0.9826	0.9861	0.9025	0.9696	0.9513	0.9409	0.9825	0.9706	0.8868	0.9009	0.8727	0.9296	0.9629	0.9793	0.9230	1.0000	0.9023	0.9737	0.9394	0.9466
D9C	0.7662	0.7837	0.7915	0.8346	0.7594	0.8128	0.9246	0.9128	0.9477	0.8953	0.9309	0.9193	0.9739	0.9572	0.8237	0.9722	0.9225	0.9535	0.9165	0.9036	0.9407	0.9774	0.9590	0.9351	0.9735	0.9023	1.0000	0.9265	0.9249	0.9667
D10A	0.8461	0.8560	0.8617	0.8140	0.8307	0.8449	0.9617	0.9815	0.9331	0.9714	0.9877	0.9773	0.9435	0.9789	0.9164	0.9619	0.9815	0.9695	0.9367	0.9490	0.9227	0.9612	0.9682	0.9746	0.9400	0.9737	0.9265	1.0000	0.9753	0.9747
D10B	0.8188	0.8441	0.8436	0.8277	0.7771	0.8508	0.9621	0.9592	0.9088	0.9299	0.9639	0.9383	0.9567	0.9584	0.8581	0.9534	0.9508	0.9386	0.9201	0.9535	0.9212	0.9560	0.9420	0.9398	0.9315	0.9394	0.9249	0.9753	1.0000	0.9734
D10C	0.8308	0.8491	0.8520	0.8447	0.8045	0.8483	0.9618	0.9642	0.9574	0.9371	0.9681	0.9546	0.9711	0.9781	0.8743	0.9752	0.9565	0.9682	0.9352	0.9556	0.9551	0.9797	0.9768	0.9665	0.9594	0.9466	0.9667	0.9747	0.9734	1.0000

Appendix C

PPMC Coefficients for the TIC and EIPs of Five Neat Diesels Analyzed in Triplicate

Table C.1 PPMC Coefficients for the TIC of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9941	0.9962	0.9405	0.9468	0.9460	0.9872	0.9878	0.9758	0.9709	0.9736	0.9728	0.9733	0.9731	0.9709
D21B	0.9941	1.0000	0.9975	0.9364	0.9450	0.9452	0.9814	0.9847	0.9698	0.9722	0.9754	0.9774	0.9681	0.9680	0.9655
D21C	0.9962	0.9975	1.0000	0.9396	0.9454	0.9462	0.9836	0.9865	0.9731	0.9770	0.9803	0.9799	0.9686	0.9679	0.9661
D22A	0.9405	0.9364	0.9396	1.0000	0.9879	0.9841	0.9351	0.9401	0.9380	0.8960	0.9006	0.8966	0.9462	0.9413	0.9418
D22B	0.9468	0.9450	0.9454	0.9879	1.0000	0.9899	0.9411	0.9465	0.9429	0.9029	0.9074	0.9048	0.9498	0.9473	0.9459
D22C	0.9460	0.9452	0.9462	0.9841	0.9899	1.0000	0.9398	0.9437	0.9383	0.9007	0.9069	0.9037	0.9458	0.9451	0.9419
D23A	0.9872	0.9814	0.9836	0.9351	0.9411	0.9398	1.0000	0.9908	0.9836	0.9631	0.9652	0.9633	0.9863	0.9854	0.9844
D23B	0.9878	0.9847	0.9865	0.9401	0.9465	0.9437	0.9908	1.0000	0.9780	0.9663	0.9699	0.9682	0.9844	0.9819	0.9816
D23C	0.9758	0.9698	0.9731	0.9380	0.9429	0.9383	0.9836	0.9780	1.0000	0.9569	0.9572	0.9538	0.9879	0.9850	0.9874
D24A	0.9709	0.9722	0.9770	0.8960	0.9029	0.9007	0.9631	0.9663	0.9569	1.0000	0.9969	0.9967	0.9427	0.9384	0.9390
D24B	0.9736	0.9754	0.9803	0.9006	0.9074	0.9069	0.9652	0.9699	0.9572	0.9969	1.0000	0.9969	0.9449	0.9411	0.9404
D24C	0.9728	0.9774	0.9799	0.8966	0.9048	0.9037	0.9633	0.9682	0.9538	0.9967	0.9969	1.0000	0.9423	0.9399	0.9391
D25A	0.9733	0.9681	0.9686	0.9462	0.9498	0.9458	0.9863	0.9844	0.9879	0.9427	0.9449	0.9423	1.0000	0.9955	0.9973
D25B	0.9731	0.9680	0.9679	0.9413	0.9473	0.9451	0.9854	0.9819	0.9850	0.9384	0.9411	0.9399	0.9955	1.0000	0.9956
D25C	0.9709	0.9655	0.9661	0.9418	0.9459	0.9419	0.9844	0.9816	0.9874	0.9390	0.9404	0.9391	0.9973	0.9956	1.0000

Table C.2 PPMC Coefficients for the Alkane EIP of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9880	0.9937	0.9299	0.9170	0.9345	0.9763	0.9151	0.9788	0.9679	0.9695	0.9700	0.9752	0.9707	0.9762
D21B	0.9880	1.0000	0.9960	0.9078	0.8921	0.9145	0.9576	0.9242	0.9558	0.9508	0.9590	0.9632	0.9625	0.9667	0.9615
D21C	0.9937	0.9960	1.0000	0.9174	0.9051	0.9256	0.9723	0.9216	0.9700	0.9647	0.9708	0.9750	0.9695	0.9687	0.9688
D22A	0.9299	0.9078	0.9174	1.0000	0.9925	0.9908	0.9446	0.8433	0.9371	0.8703	0.8669	0.8708	0.9489	0.9174	0.9423
D22B	0.9170	0.8921	0.9051	0.9925	1.0000	0.9866	0.9392	0.8334	0.9308	0.8620	0.8586	0.8668	0.9348	0.8999	0.9249
D22C	0.9345	0.9145	0.9256	0.9908	0.9866	1.0000	0.9414	0.8499	0.9292	0.8686	0.8673	0.8748	0.9424	0.9199	0.9374
D23A	0.9763	0.9576	0.9723	0.9446	0.9392	0.9414	1.0000	0.8869	0.9917	0.9736	0.9728	0.9747	0.9790	0.9534	0.9779
D23B	0.9151	0.9242	0.9216	0.8433	0.8334	0.8499	0.8869	1.0000	0.8788	0.8687	0.8760	0.8886	0.8823	0.8826	0.8814
D23C	0.9788	0.9558	0.9700	0.9371	0.9308	0.9292	0.9917	0.8788	1.0000	0.9815	0.9779	0.9702	0.9809	0.9530	0.9781
D24A	0.9679	0.9508	0.9647	0.8703	0.8620	0.8686	0.9736	0.8687	0.9815	1.0000	0.9971	0.9895	0.9628	0.9354	0.9629
D24B	0.9695	0.9590	0.9708	0.8669	0.8586	0.8673	0.9728	0.8760	0.9779	0.9971	1.0000	0.9923	0.9635	0.9405	0.9622
D24C	0.9700	0.9632	0.9750	0.8708	0.8668	0.8748	0.9747	0.8886	0.9702	0.9895	0.9923	1.0000	0.9589	0.9370	0.9581
D25A	0.9752	0.9625	0.9695	0.9489	0.9348	0.9424	0.9790	0.8823	0.9809	0.9628	0.9635	0.9589	1.0000	0.9577	0.9912
D25B	0.9707	0.9667	0.9687	0.9174	0.8999	0.9199	0.9534	0.8826	0.9530	0.9354	0.9405	0.9370	0.9577	1.0000	0.9604
D25C	0.9762	0.9615	0.9688	0.9423	0.9249	0.9374	0.9779	0.8814	0.9781	0.9629	0.9622	0.9581	0.9912	0.9604	1.0000

Table C.3 PPMC Coefficients for the Aromatic EIP of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9642	0.9660	0.8503	0.8502	0.8487	0.9702	0.9705	0.9524	0.9577	0.9562	0.9538	0.9349	0.9564	0.9522
D21B	0.9642	1.0000	0.9972	0.8974	0.9022	0.9080	0.9460	0.9453	0.9766	0.9835	0.9868	0.9874	0.9600	0.9339	0.9265
D21C	0.9660	0.9972	1.0000	0.9011	0.9050	0.9097	0.9473	0.9447	0.9783	0.9855	0.9861	0.9849	0.9610	0.9345	0.9271
D22A	0.8503	0.8974	0.9011	1.0000	0.9930	0.9895	0.7954	0.8033	0.8543	0.8531	0.8513	0.8496	0.8376	0.7881	0.7768
D22B	0.8502	0.9022	0.9050	0.9930	1.0000	0.9933	0.7984	0.8041	0.8584	0.8583	0.8567	0.8560	0.8406	0.7914	0.7796
D22C	0.8487	0.9080	0.9097	0.9895	0.9933	1.0000	0.8009	0.8035	0.8581	0.8581	0.8615	0.8615	0.8437	0.7931	0.7811
D23A	0.9702	0.9460	0.9473	0.7954	0.7984	0.8009	1.0000	0.9803	0.9637	0.9568	0.9560	0.9551	0.9566	0.9857	0.9935
D23B	0.9705	0.9453	0.9447	0.8033	0.8041	0.8035	0.9803	1.0000	0.9674	0.9569	0.9522	0.9518	0.9604	0.9827	0.9763
D23C	0.9524	0.9766	0.9783	0.8543	0.8584	0.8581	0.9637	0.9674	1.0000	0.9863	0.9822	0.9815	0.9891	0.9675	0.9581
D24A	0.9577	0.9835	0.9855	0.8531	0.8583	0.8581	0.9568	0.9569	0.9863	1.0000	0.9948	0.9941	0.9692	0.9493	0.9423
D24B	0.9562	0.9868	0.9861	0.8513	0.8567	0.8615	0.9560	0.9522	0.9822	0.9948	1.0000	0.9984	0.9701	0.9470	0.9410
D24C	0.9538	0.9874	0.9849	0.8496	0.8560	0.8615	0.9551	0.9518	0.9815	0.9941	0.9984	1.0000	0.9700	0.9468	0.9405
D25A	0.9349	0.9600	0.9610	0.8376	0.8406	0.8437	0.9566	0.9604	0.9891	0.9692	0.9701	0.9700	1.0000	0.9686	0.9597
D25B	0.9564	0.9339	0.9345	0.7881	0.7914	0.7931	0.9857	0.9827	0.9675	0.9493	0.9470	0.9468	0.9686	1.0000	0.9886
D25C	0.9522	0.9265	0.9271	0.7768	0.7796	0.7811	0.9935	0.9763	0.9581	0.9423	0.9410	0.9405	0.9597	0.9886	1.0000

Table C.4 PPMC Coefficients for the Indane EIP of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9943	0.9952	0.9416	0.9411	0.9388	0.9911	0.9927	0.9935	0.9926	0.9916	0.9910	0.9863	0.9849	0.9856
D21B	0.9943	1.0000	0.9979	0.9436	0.9410	0.9421	0.9915	0.9874	0.9914	0.9907	0.9928	0.9935	0.9857	0.9836	0.9840
D21C	0.9952	0.9979	1.0000	0.9431	0.9456	0.9456	0.9916	0.9891	0.9918	0.9914	0.9947	0.9949	0.9857	0.9854	0.9843
D22A	0.9416	0.9436	0.9431	1.0000	0.9916	0.9929	0.9313	0.9323	0.9317	0.9321	0.9279	0.9281	0.9252	0.9242	0.9257
D22B	0.9411	0.9410	0.9456	0.9916	1.0000	0.9967	0.9274	0.9296	0.9303	0.9291	0.9300	0.9294	0.9228	0.9226	0.9220
D22C	0.9388	0.9421	0.9456	0.9929	0.9967	1.0000	0.9293	0.9291	0.9298	0.9301	0.9297	0.9297	0.9229	0.9249	0.9243
D23A	0.9911	0.9915	0.9916	0.9313	0.9274	0.9293	1.0000	0.9962	0.9959	0.9949	0.9943	0.9936	0.9950	0.9952	0.9957
D23B	0.9927	0.9874	0.9891	0.9323	0.9296	0.9291	0.9962	1.0000	0.9961	0.9947	0.9925	0.9914	0.9940	0.9944	0.9952
D23C	0.9935	0.9914	0.9918	0.9317	0.9303	0.9298	0.9959	0.9961	1.0000	0.9943	0.9942	0.9934	0.9963	0.9948	0.9951
D24A	0.9926	0.9907	0.9914	0.9321	0.9291	0.9301	0.9949	0.9947	0.9943	1.0000	0.9965	0.9956	0.9896	0.9894	0.9905
D24B	0.9916	0.9928	0.9947	0.9279	0.9300	0.9297	0.9943	0.9925	0.9942	0.9965	1.0000	0.9987	0.9902	0.9899	0.9891
D24C	0.9910	0.9935	0.9949	0.9281	0.9294	0.9297	0.9936	0.9914	0.9934	0.9956	0.9987	1.0000	0.9896	0.9896	0.9885
D25A	0.9863	0.9857	0.9857	0.9252	0.9228	0.9229	0.9950	0.9940	0.9963	0.9896	0.9902	0.9896	1.0000	0.9967	0.9978
D25B	0.9849	0.9836	0.9854	0.9242	0.9226	0.9249	0.9952	0.9944	0.9948	0.9894	0.9899	0.9896	0.9967	1.0000	0.9976
D25C	0.9856	0.9840	0.9843	0.9257	0.9220	0.9243	0.9957	0.9952	0.9951	0.9905	0.9891	0.9885	0.9978	0.9976	1.0000

Table C.5 PPMC Coefficients for the OCP EIP of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9923	0.9948	0.9474	0.9348	0.9507	0.9831	0.9739	0.9815	0.9589	0.9593	0.9522	0.9753	0.9783	0.9620
D21B	0.9923	1.0000	0.9971	0.9354	0.9267	0.9404	0.9788	0.9666	0.9804	0.9628	0.9664	0.9623	0.9744	0.9758	0.9609
D21C	0.9948	0.9971	1.0000	0.9383	0.9269	0.9430	0.9825	0.9705	0.9816	0.9674	0.9703	0.9651	0.9741	0.9761	0.9609
D22A	0.9474	0.9354	0.9383	1.0000	0.9798	0.9973	0.9452	0.9368	0.9339	0.8578	0.8579	0.8463	0.9407	0.9453	0.9322
D22B	0.9348	0.9267	0.9269	0.9798	1.0000	0.9791	0.9324	0.9216	0.9463	0.8540	0.8553	0.8445	0.9361	0.9375	0.9243
D22C	0.9507	0.9404	0.9430	0.9973	0.9791	1.0000	0.9474	0.9392	0.9356	0.8634	0.8644	0.8538	0.9436	0.9480	0.9355
D23A	0.9831	0.9788	0.9825	0.9452	0.9324	0.9474	1.0000	0.9831	0.9819	0.9537	0.9555	0.9544	0.9859	0.9878	0.9733
D23B	0.9739	0.9666	0.9705	0.9368	0.9216	0.9392	0.9831	1.0000	0.9682	0.9475	0.9470	0.9449	0.9768	0.9784	0.9629
D23C	0.9815	0.9804	0.9816	0.9339	0.9463	0.9356	0.9819	0.9682	1.0000	0.9591	0.9610	0.9553	0.9812	0.9809	0.9674
D24A	0.9589	0.9628	0.9674	0.8578	0.8540	0.8634	0.9537	0.9475	0.9591	1.0000	0.9963	0.9863	0.9406	0.9395	0.9200
D24B	0.9593	0.9664	0.9703	0.8579	0.8553	0.8644	0.9555	0.9470	0.9610	0.9963	1.0000	0.9906	0.9441	0.9429	0.9224
D24C	0.9522	0.9623	0.9651	0.8463	0.8445	0.8538	0.9544	0.9449	0.9553	0.9863	0.9906	1.0000	0.9462	0.9448	0.9276
D25A	0.9753	0.9744	0.9741	0.9407	0.9361	0.9436	0.9859	0.9768	0.9812	0.9406	0.9441	0.9462	1.0000	0.9946	0.9793
D25B	0.9783	0.9758	0.9761	0.9453	0.9375	0.9480	0.9878	0.9784	0.9809	0.9395	0.9429	0.9448	0.9946	1.0000	0.9828
D25C	0.9620	0.9609	0.9609	0.9322	0.9243	0.9355	0.9733	0.9629	0.9674	0.9200	0.9224	0.9276	0.9793	0.9828	1.0000

Table C.6 PPMC Coefficients for the PNA EIP of Triplicate Analyses of Diesels 21-25

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9927	0.9942	0.9503	0.9501	0.9498	0.9825	0.9808	0.9819	0.9886	0.9843	0.9813	0.9716	0.9752	0.9653
D21B	0.9927	1.0000	0.9983	0.9475	0.9467	0.9484	0.9803	0.9760	0.9799	0.9799	0.9896	0.9839	0.9706	0.9727	0.9682
D21C	0.9942	0.9983	1.0000	0.9483	0.9479	0.9491	0.9820	0.9786	0.9811	0.9814	0.9903	0.9849	0.9701	0.9719	0.9670
D22A	0.9503	0.9475	0.9483	1.0000	0.9888	0.9887	0.9286	0.9286	0.9308	0.9399	0.9392	0.9273	0.9374	0.9402	0.9298
D22B	0.9501	0.9467	0.9479	0.9888	1.0000	0.9923	0.9334	0.9296	0.9338	0.9358	0.9320	0.9325	0.9321	0.9347	0.9283
D22C	0.9498	0.9484	0.9491	0.9887	0.9923	1.0000	0.9303	0.9267	0.9315	0.9380	0.9380	0.9300	0.9412	0.9398	0.9348
D23A	0.9825	0.9803	0.9820	0.9286	0.9334	0.9303	1.0000	0.9971	0.9985	0.9802	0.9750	0.9807	0.9757	0.9801	0.9772
D23B	0.9808	0.9760	0.9786	0.9286	0.9296	0.9267	0.9971	1.0000	0.9956	0.9819	0.9739	0.9778	0.9726	0.9775	0.9748
D23C	0.9819	0.9799	0.9811	0.9308	0.9338	0.9315	0.9985	0.9956	1.0000	0.9802	0.9757	0.9792	0.9791	0.9834	0.9795
D24A	0.9886	0.9799	0.9814	0.9399	0.9358	0.9380	0.9802	0.9819	0.9802	1.0000	0.9814	0.9772	0.9743	0.9771	0.9665
D24B	0.9843	0.9896	0.9903	0.9392	0.9320	0.9380	0.9750	0.9739	0.9757	0.9814	1.0000	0.9822	0.9755	0.9737	0.9682
D24C	0.9813	0.9839	0.9849	0.9273	0.9325	0.9300	0.9807	0.9778	0.9792	0.9772	0.9822	1.0000	0.9626	0.9664	0.9703
D25A	0.9716	0.9706	0.9701	0.9374	0.9321	0.9412	0.9757	0.9726	0.9791	0.9743	0.9755	0.9626	1.0000	0.9961	0.9909
D25B	0.9752	0.9727	0.9719	0.9402	0.9347	0.9398	0.9801	0.9775	0.9834	0.9771	0.9737	0.9664	0.9961	1.0000	0.9907
D25C	0.9653	0.9682	0.9670	0.9298	0.9283	0.9348	0.9772	0.9748	0.9795	0.9665	0.9682	0.9703	0.9909	0.9907	1.0000

Appendix D

PPMC Coefficients for the TIC and EIPs of Compiled Neat and Burned Diesels

Table D.1 PPMC Coefficients for the TIC of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9941	0.9962	0.9405	0.9468	0.9460	0.9872	0.9878	0.9758	0.9709	0.9736	0.9728	0.9733	0.9731	0.9709
D21B	0.9941	1.0000	0.9975	0.9364	0.9450	0.9452	0.9814	0.9847	0.9698	0.9722	0.9754	0.9774	0.9681	0.9680	0.9655
D21C	0.9962	0.9975	1.0000	0.9396	0.9454	0.9462	0.9836	0.9865	0.9731	0.9770	0.9803	0.9799	0.9686	0.9679	0.9661
D22A	0.9405	0.9364	0.9396	1.0000	0.9879	0.9841	0.9351	0.9401	0.9380	0.8960	0.9006	0.8966	0.9462	0.9413	0.9418
D22B	0.9468	0.9450	0.9454	0.9879	1.0000	0.9899	0.9411	0.9465	0.9429	0.9029	0.9074	0.9048	0.9498	0.9473	0.9459
D22C	0.9460	0.9452	0.9462	0.9841	0.9899	1.0000	0.9398	0.9437	0.9383	0.9007	0.9069	0.9037	0.9458	0.9451	0.9419
D23A	0.9872	0.9814	0.9836	0.9351	0.9411	0.9398	1.0000	0.9908	0.9836	0.9631	0.9652	0.9633	0.9863	0.9854	0.9844
D23B	0.9878	0.9847	0.9865	0.9401	0.9465	0.9437	0.9908	1.0000	0.9780	0.9663	0.9699	0.9682	0.9844	0.9819	0.9816
D23C	0.9758	0.9698	0.9731	0.9380	0.9429	0.9383	0.9836	0.9780	1.0000	0.9569	0.9572	0.9538	0.9879	0.9850	0.9874
D24A	0.9709	0.9722	0.9770	0.8960	0.9029	0.9007	0.9631	0.9663	0.9569	1.0000	0.9969	0.9967	0.9427	0.9384	0.9390
D24B	0.9736	0.9754	0.9803	0.9006	0.9074	0.9069	0.9652	0.9699	0.9572	0.9969	1.0000	0.9969	0.9449	0.9411	0.9404
D24C	0.9728	0.9774	0.9799	0.8966	0.9048	0.9037	0.9633	0.9682	0.9538	0.9967	0.9969	1.0000	0.9423	0.9399	0.9391
D25A	0.9733	0.9681	0.9686	0.9462	0.9498	0.9458	0.9863	0.9844	0.9879	0.9427	0.9449	0.9423	1.0000	0.9955	0.9973
D25B	0.9731	0.9680	0.9679	0.9413	0.9473	0.9451	0.9854	0.9819	0.9850	0.9384	0.9411	0.9399	0.9955	1.0000	0.9956
D25C	0.9709	0.9655	0.9661	0.9418	0.9459	0.9419	0.9844	0.9816	0.9874	0.9390	0.9404	0.9391	0.9973	0.9956	1.0000
Cloth A	0.8891	0.8699	0.8833	0.8771	0.8635	0.8616	0.8961	0.8945	0.9024	0.8775	0.8799	0.8618	0.8951	0.8785	0.8865
Cloth B	0.8815	0.8600	0.8739	0.8718	0.8570	0.8553	0.8885	0.8849	0.8936	0.8575	0.8610	0.8412	0.8870	0.8705	0.8786
Cloth C	0.8570	0.8322	0.8449	0.8585	0.8418	0.8402	0.8668	0.8614	0.8677	0.8010	0.8068	0.7858	0.8701	0.8550	0.8623
Mag A	0.8431	0.8200	0.8330	0.8530	0.8362	0.8348	0.8516	0.8491	0.8539	0.7904	0.7967	0.7757	0.8552	0.8397	0.8469
Mag B	0.7066	0.6769	0.6873	0.7302	0.7099	0.7093	0.7188	0.7084	0.7077	0.5826	0.5948	0.5706	0.7279	0.7179	0.7231
Mag C	0.8817	0.8590	0.8717	0.8823	0.8671	0.8654	0.8901	0.8862	0.8896	0.8291	0.8343	0.8149	0.8921	0.8775	0.8844
Car A	0.3908	0.3594	0.3716	0.3981	0.3778	0.3786	0.3929	0.3743	0.3732	0.2552	0.2695	0.2452	0.3836	0.3810	0.3823
Car B	0.6824	0.6541	0.6672	0.7021	0.6823	0.6825	0.6869	0.6778	0.6770	0.5738	0.5856	0.5608	0.6859	0.6741	0.6794
Car C	0.7806	0.7533	0.7660	0.8005	0.7809	0.7798	0.7861	0.7801	0.7828	0.6928	0.7019	0.6788	0.7891	0.7747	0.7820
B-A Cl	0.8420	0.8203	0.8300	0.8781	0.8620	0.8592	0.8503	0.8522	0.8512	0.7746	0.7817	0.7633	0.8642	0.8510	0.8574
B-B Cl	0.8813	0.8593	0.8686	0.8842	0.8712	0.8699	0.8991	0.8947	0.8996	0.8268	0.8312	0.8149	0.9133	0.9020	0.9075
B-A Mag	0.8257	0.8117	0.8195	0.8642	0.8521	0.8561	0.8333	0.8366	0.8378	0.7780	0.7852	0.7683	0.8520	0.8396	0.8459
B-B Mag	-0.1739	-0.1591	-0.1724	-0.2219	-0.2054	-0.2060	-0.1655	-0.1641	-0.1649	-0.1244	-0.1319	-0.1149	-0.1464	-0.1388	-0.1402
B-A Car	0.8059	0.7806	0.7915	0.8454	0.8285	0.8279	0.8119	0.8049	0.8047	0.7060	0.7157	0.6952	0.8198	0.8090	0.8143
B-B Car	0.1797	0.1771	0.1726	0.1901	0.1857	0.1859	0.1970	0.1953	0.1932	0.1689	0.1618	0.1705	0.2177	0.2185	0.2190

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.8891	0.8815	0.8570	0.8431	0.7066	0.8817	0.3908	0.6824	0.7806	0.8420	0.8813	0.8257	-0.1739	0.8059	0.1797
D21B	0.8699	0.8600	0.8322	0.8200	0.6769	0.8590	0.3594	0.6541	0.7533	0.8203	0.8593	0.8117	-0.1591	0.7806	0.1771
D21C	0.8833	0.8739	0.8449	0.8330	0.6873	0.8717	0.3716	0.6672	0.7660	0.8300	0.8686	0.8195	-0.1724	0.7915	0.1726
D22A	0.8771	0.8718	0.8585	0.8530	0.7302	0.8823	0.3981	0.7021	0.8005	0.8781	0.8842	0.8642	-0.2219	0.8454	0.1901
D22B	0.8635	0.8570	0.8418	0.8362	0.7099	0.8671	0.3778	0.6823	0.7809	0.8620	0.8712	0.8521	-0.2054	0.8285	0.1857
D22C	0.8616	0.8553	0.8402	0.8348	0.7093	0.8654	0.3786	0.6825	0.7798	0.8592	0.8699	0.8561	-0.2060	0.8279	0.1859
D23A	0.8961	0.8885	0.8668	0.8516	0.7188	0.8901	0.3929	0.6869	0.7861	0.8503	0.8991	0.8333	-0.1655	0.8119	0.1970
D23B	0.8945	0.8849	0.8614	0.8491	0.7084	0.8862	0.3743	0.6778	0.7801	0.8522	0.8947	0.8366	-0.1641	0.8049	0.1953
D23C	0.9024	0.8936	0.8677	0.8539	0.7077	0.8896	0.3732	0.6770	0.7828	0.8512	0.8996	0.8378	-0.1649	0.8047	0.1932
D24A	0.8775	0.8575	0.8010	0.7904	0.5826	0.8291	0.2552	0.5738	0.6928	0.7746	0.8268	0.7780	-0.1244	0.7060	0.1689
D24B	0.8799	0.8610	0.8068	0.7967	0.5948	0.8343	0.2695	0.5856	0.7019	0.7817	0.8312	0.7852	-0.1319	0.7157	0.1618
D24C	0.8618	0.8412	0.7858	0.7757	0.5706	0.8149	0.2452	0.5608	0.6788	0.7633	0.8149	0.7683	-0.1149	0.6952	0.1705
D25A	0.8951	0.8870	0.8701	0.8552	0.7279	0.8921	0.3836	0.6859	0.7891	0.8642	0.9133	0.8520	-0.1464	0.8198	0.2177
D25B	0.8785	0.8705	0.8550	0.8397	0.7179	0.8775	0.3810	0.6741	0.7747	0.8510	0.9020	0.8396	-0.1388	0.8090	0.2185
D25C	0.8865	0.8786	0.8623	0.8469	0.7231	0.8844	0.3823	0.6794	0.7820	0.8574	0.9075	0.8459	-0.1402	0.8143	0.2190
Cloth A	1.0000	0.9961	0.9729	0.9668	0.8045	0.9758	0.4427	0.7878	0.8953	0.9486	0.9667	0.9095	-0.3180	0.8866	0.1533
Cloth B	0.9961	1.0000	0.9851	0.9768	0.8418	0.9851	0.5052	0.8245	0.9185	0.9565	0.9723	0.9132	-0.3444	0.9111	0.1471
Cloth C	0.9729	0.9851	1.0000	0.9874	0.9149	0.9955	0.5988	0.8871	0.9567	0.9731	0.9808	0.9117	-0.3760	0.9524	0.1548
Mag A	0.9668	0.9768	0.9874	1.0000	0.9078	0.9895	0.5763	0.8829	0.9547	0.9699	0.9706	0.9086	-0.4550	0.9454	0.1134
Mag B	0.8045	0.8418	0.9149	0.9078	1.0000	0.9058	0.8054	0.9590	0.9496	0.8936	0.8820	0.8135	-0.4767	0.9575	0.0867
Mag C	0.9758	0.9851	0.9955	0.9895	0.9058	1.0000	0.5759	0.8782	0.9530	0.9740	0.9821	0.9163	-0.3733	0.9512	0.1500
Car A	0.4427	0.5052	0.5988	0.5763	0.8054	0.5759	1.0000	0.8473	0.7151	0.5415	0.5341	0.4805	-0.5007	0.7346	-0.0751
Car B	0.7878	0.8245	0.8871	0.8829	0.9590	0.8782	0.8473	1.0000	0.9609	0.8591	0.8405	0.7920	-0.5481	0.9469	-0.0012
Car C	0.8953	0.9185	0.9567	0.9547	0.9496	0.9530	0.7151	0.9609	1.0000	0.9423	0.9266	0.8705	-0.4708	0.9708	0.0699
B-A Cl	0.9486	0.9565	0.9731	0.9699	0.8936	0.9740	0.5415	0.8591	0.9423	1.0000	0.9694	0.9257	-0.3681	0.9545	0.1714
B-B Cl	0.9667	0.9723	0.9808	0.9706	0.8820	0.9821	0.5341	0.8405	0.9266	0.9694	1.0000	0.9218	-0.3245	0.9379	0.1793
B-A Mag	0.9095	0.9132	0.9117	0.9086	0.8135	0.9163	0.4805	0.7920	0.8705	0.9257	0.9218	1.0000	-0.2864	0.8907	0.1726
B-B Mag	-0.3180	-0.3444	-0.3760	-0.4550	-0.4767	-0.3733	-0.5007	-0.5481	-0.4708	-0.3681	-0.3245	-0.2864	1.0000	-0.4497	0.3735
B-A Car	0.8866	0.9111	0.9524	0.9454	0.9575	0.9512	0.7346	0.9469	0.9708	0.9545	0.9379	0.8907	-0.4497	1.0000	0.0934
B-B Car	0.1533	0.1471	0.1548	0.1134	0.0867	0.1500	-0.0751	-0.0012	0.0699	0.1714	0.1793	0.1726	0.3735	0.0934	1.0000

Table D.2 PPMC Coefficients for the Alkane EIP of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9880	0.9937	0.9299	0.9170	0.9345	0.9763	0.9151	0.9788	0.9679	0.9695	0.9700	0.9752	0.9707	0.9762
D21B	0.9880	1.0000	0.9960	0.9078	0.8921	0.9145	0.9576	0.9242	0.9558	0.9508	0.9590	0.9632	0.9625	0.9667	0.9615
D21C	0.9937	0.9960	1.0000	0.9174	0.9051	0.9256	0.9723	0.9216	0.9700	0.9647	0.9708	0.9750	0.9695	0.9687	0.9688
D22A	0.9299	0.9078	0.9174	1.0000	0.9925	0.9908	0.9446	0.8433	0.9371	0.8703	0.8669	0.8708	0.9489	0.9174	0.9423
D22B	0.9170	0.8921	0.9051	0.9925	1.0000	0.9866	0.9392	0.8334	0.9308	0.8620	0.8586	0.8668	0.9348	0.8999	0.9249
D22C	0.9345	0.9145	0.9256	0.9908	0.9866	1.0000	0.9414	0.8499	0.9292	0.8686	0.8673	0.8748	0.9424	0.9199	0.9374
D23A	0.9763	0.9576	0.9723	0.9446	0.9392	0.9414	1.0000	0.8869	0.9917	0.9736	0.9728	0.9747	0.9790	0.9534	0.9779
D23B	0.9151	0.9242	0.9216	0.8433	0.8334	0.8499	0.8869	1.0000	0.8788	0.8687	0.8760	0.8886	0.8823	0.8826	0.8814
D23C	0.9788	0.9558	0.9700	0.9371	0.9308	0.9292	0.9917	0.8788	1.0000	0.9815	0.9779	0.9702	0.9809	0.9530	0.9781
D24A	0.9679	0.9508	0.9647	0.8703	0.8620	0.8686	0.9736	0.8687	0.9815	1.0000	0.9971	0.9895	0.9628	0.9354	0.9629
D24B	0.9695	0.9590	0.9708	0.8669	0.8586	0.8673	0.9728	0.8760	0.9779	0.9971	1.0000	0.9923	0.9635	0.9405	0.9622
D24C	0.9700	0.9632	0.9750	0.8708	0.8668	0.8748	0.9747	0.8886	0.9702	0.9895	0.9923	1.0000	0.9589	0.9370	0.9581
D25A	0.9752	0.9625	0.9695	0.9489	0.9348	0.9424	0.9790	0.8823	0.9809	0.9628	0.9635	0.9589	1.0000	0.9577	0.9912
D25B	0.9707	0.9667	0.9687	0.9174	0.8999	0.9199	0.9534	0.8826	0.9530	0.9354	0.9405	0.9370	0.9577	1.0000	0.9604
D25C	0.9762	0.9615	0.9688	0.9423	0.9249	0.9374	0.9779	0.8814	0.9781	0.9629	0.9622	0.9581	0.9912	0.9604	1.0000
Cloth A	0.7885	0.7314	0.7628	0.8188	0.8366	0.8233	0.8474	0.6780	0.8426	0.8074	0.7940	0.7876	0.8051	0.7494	0.7970
Cloth B	0.7795	0.7220	0.7530	0.8213	0.8398	0.8269	0.8366	0.6746	0.8299	0.7878	0.7752	0.7676	0.7945	0.7414	0.7868
Cloth C	0.7656	0.7085	0.7368	0.8429	0.8597	0.8501	0.8197	0.6635	0.8079	0.7471	0.7353	0.7313	0.7867	0.7304	0.7752
Mag A	0.7545	0.6984	0.7266	0.8373	0.8553	0.8465	0.8081	0.6574	0.7939	0.7327	0.7209	0.7186	0.7762	0.7177	0.7656
Mag B	0.6664	0.6152	0.6352	0.8040	0.8172	0.8191	0.7014	0.5941	0.6761	0.5836	0.5768	0.5784	0.6888	0.6392	0.6759
Mag C	0.8195	0.7648	0.7911	0.8872	0.8918	0.8899	0.8649	0.7087	0.8587	0.7999	0.7884	0.7786	0.8418	0.7855	0.8320
Car A	0.5015	0.4609	0.4724	0.6270	0.6351	0.6443	0.5111	0.4576	0.4874	0.3885	0.3897	0.3839	0.5113	0.4918	0.4970
Car B	0.6763	0.6255	0.6460	0.8067	0.8193	0.8202	0.7107	0.6016	0.6879	0.5978	0.5910	0.5891	0.6970	0.6499	0.6858
Car C	0.7122	0.6576	0.6820	0.8323	0.8467	0.8430	0.7578	0.6254	0.7381	0.6567	0.6468	0.6460	0.7359	0.6794	0.7249
B-A Cl	0.7284	0.6762	0.7001	0.8577	0.8707	0.8700	0.7746	0.6407	0.7536	0.6731	0.6633	0.6634	0.7594	0.7024	0.7483
B-B Cl	0.7825	0.7258	0.7544	0.8543	0.8693	0.8619	0.8346	0.6849	0.8239	0.7644	0.7529	0.7469	0.8042	0.7535	0.7964
B-A Mag	0.7414	0.6868	0.7120	0.8303	0.8509	0.8459	0.7855	0.6430	0.7663	0.7043	0.6938	0.6964	0.7632	0.7050	0.7554
B-B Mag	-0.5063	-0.4619	-0.4799	-0.6334	-0.6472	-0.6513	-0.5305	-0.4551	-0.5054	-0.4202	-0.4164	-0.4171	-0.5192	-0.4832	-0.5071
B-A Car	0.6856	0.6355	0.6558	0.8234	0.8339	0.8375	0.7179	0.6143	0.6947	0.5991	0.5924	0.5927	0.7080	0.6633	0.6976
B-B Car	0.3337	0.3044	0.3130	0.4138	0.4185	0.4256	0.3340	0.2947	0.3240	0.2587	0.2593	0.2481	0.3379	0.3218	0.3304

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.7885	0.7795	0.7656	0.7545	0.6664	0.8195	0.5015	0.6763	0.7122	0.7284	0.7825	0.7414	-0.5063	0.6856	0.3337
D21B	0.7314	0.7220	0.7085	0.6984	0.6152	0.7648	0.4609	0.6255	0.6576	0.6762	0.7258	0.6868	-0.4619	0.6355	0.3044
D21C	0.7628	0.7530	0.7368	0.7266	0.6352	0.7911	0.4724	0.6460	0.6820	0.7001	0.7544	0.7120	-0.4799	0.6558	0.3130
D22A	0.8188	0.8213	0.8429	0.8373	0.8040	0.8872	0.6270	0.8067	0.8323	0.8577	0.8543	0.8303	-0.6334	0.8234	0.4138
D22B	0.8366	0.8398	0.8597	0.8553	0.8172	0.8918	0.6351	0.8193	0.8467	0.8707	0.8693	0.8509	-0.6472	0.8339	0.4185
D22C	0.8233	0.8269	0.8501	0.8465	0.8191	0.8899	0.6443	0.8202	0.8430	0.8700	0.8619	0.8459	-0.6513	0.8375	0.4256
D23A	0.8474	0.8366	0.8197	0.8081	0.7014	0.8649	0.5111	0.7107	0.7578	0.7746	0.8346	0.7855	-0.5305	0.7179	0.3340
D23B	0.6780	0.6746	0.6635	0.6574	0.5941	0.7087	0.4576	0.6016	0.6254	0.6407	0.6849	0.6430	-0.4551	0.6143	0.2947
D23C	0.8426	0.8299	0.8079	0.7939	0.6761	0.8587	0.4874	0.6879	0.7381	0.7536	0.8239	0.7663	-0.5054	0.6947	0.3240
D24A	0.8074	0.7878	0.7471	0.7327	0.5836	0.7999	0.3885	0.5978	0.6567	0.6731	0.7644	0.7043	-0.4202	0.5991	0.2587
D24B	0.7940	0.7752	0.7353	0.7209	0.5768	0.7884	0.3897	0.5910	0.6468	0.6633	0.7529	0.6938	-0.4164	0.5924	0.2593
D24C	0.7876	0.7676	0.7313	0.7186	0.5784	0.7786	0.3839	0.5891	0.6460	0.6634	0.7469	0.6964	-0.4171	0.5927	0.2481
D25A	0.8051	0.7945	0.7867	0.7762	0.6888	0.8418	0.5113	0.6970	0.7359	0.7594	0.8042	0.7632	-0.5192	0.7080	0.3379
D25B	0.7494	0.7414	0.7304	0.7177	0.6392	0.7855	0.4918	0.6499	0.6794	0.7024	0.7535	0.7050	-0.4832	0.6633	0.3218
D25C	0.7970	0.7868	0.7752	0.7656	0.6759	0.8320	0.4970	0.6858	0.7249	0.7483	0.7964	0.7554	-0.5071	0.6976	0.3304
Cloth A	1.0000	0.9957	0.9806	0.9740	0.8493	0.9728	0.6155	0.8492	0.9194	0.9160	0.9774	0.9356	-0.6762	0.8427	0.4141
Cloth B	0.9957	1.0000	0.9887	0.9833	0.8788	0.9781	0.6652	0.8809	0.9396	0.9348	0.9871	0.9474	-0.7159	0.8731	0.4541
Cloth C	0.9806	0.9887	1.0000	0.9966	0.9316	0.9873	0.7332	0.9290	0.9742	0.9701	0.9927	0.9711	-0.7705	0.9243	0.4993
Mag A	0.9740	0.9833	0.9966	1.0000	0.9411	0.9836	0.7416	0.9377	0.9808	0.9759	0.9896	0.9763	-0.7938	0.9330	0.5205
Mag B	0.8493	0.8788	0.9316	0.9411	1.0000	0.9172	0.8925	0.9912	0.9817	0.9738	0.9226	0.9518	-0.8867	0.9913	0.6321
Mag C	0.9728	0.9781	0.9873	0.9836	0.9172	1.0000	0.7148	0.9158	0.9608	0.9623	0.9851	0.9551	-0.7515	0.9143	0.4927
Car A	0.6155	0.6652	0.7332	0.7416	0.8925	0.7148	1.0000	0.9101	0.8279	0.7918	0.7275	0.7696	-0.8952	0.9060	0.7894
Car B	0.8492	0.8809	0.9290	0.9377	0.9912	0.9158	0.9101	1.0000	0.9815	0.9665	0.9222	0.9444	-0.8976	0.9928	0.6959
Car C	0.9194	0.9396	0.9742	0.9808	0.9817	0.9608	0.8279	0.9815	1.0000	0.9889	0.9656	0.9723	-0.8477	0.9781	0.6095
B-A Cl	0.9160	0.9348	0.9701	0.9759	0.9738	0.9623	0.7918	0.9665	0.9889	1.0000	0.9679	0.9776	-0.8195	0.9707	0.5414
B-B Cl	0.9774	0.9871	0.9927	0.9896	0.9226	0.9851	0.7275	0.9222	0.9656	0.9679	1.0000	0.9686	-0.7601	0.9231	0.4925
B-A Mag	0.9356	0.9474	0.9711	0.9763	0.9518	0.9551	0.7696	0.9444	0.9723	0.9776	0.9686	1.0000	-0.7962	0.9458	0.5219
B-B Mag	-0.6762	-0.7159	-0.7705	-0.7938	-0.8867	-0.7515	-0.8952	-0.8976	-0.8477	-0.8195	-0.7601	-0.7962	1.0000	-0.8876	-0.7953
B-A Car	0.8427	0.8731	0.9243	0.9330	0.9913	0.9143	0.9060	0.9928	0.9781	0.9707	0.9231	0.9458	-0.8876	1.0000	0.6672
B-B Car	0.4141	0.4541	0.4993	0.5205	0.6321	0.4927	0.7894	0.6959	0.6095	0.5414	0.4925	0.5219	-0.7953	0.6672	1.0000

Table D.3 PPMC Coefficients for the Aromatic of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9642	0.9660	0.8503	0.8502	0.8487	0.9702	0.9705	0.9524	0.9577	0.9562	0.9538	0.9349	0.9564	0.9522
D21B	0.9642	1.0000	0.9972	0.8974	0.9022	0.9080	0.9460	0.9453	0.9766	0.9835	0.9868	0.9874	0.9600	0.9339	0.9265
D21C	0.9660	0.9972	1.0000	0.9011	0.9050	0.9097	0.9473	0.9447	0.9783	0.9855	0.9861	0.9849	0.9610	0.9345	0.9271
D22A	0.8503	0.8974	0.9011	1.0000	0.9930	0.9895	0.7954	0.8033	0.8543	0.8531	0.8513	0.8496	0.8376	0.7881	0.7768
D22B	0.8502	0.9022	0.9050	0.9930	1.0000	0.9933	0.7984	0.8041	0.8584	0.8583	0.8567	0.8560	0.8406	0.7914	0.7796
D22C	0.8487	0.9080	0.9097	0.9895	0.9933	1.0000	0.8009	0.8035	0.8581	0.8581	0.8615	0.8615	0.8437	0.7931	0.7811
D23A	0.9702	0.9460	0.9473	0.7954	0.7984	0.8009	1.0000	0.9803	0.9637	0.9568	0.9560	0.9551	0.9566	0.9857	0.9935
D23B	0.9705	0.9453	0.9447	0.8033	0.8041	0.8035	0.9803	1.0000	0.9674	0.9569	0.9522	0.9518	0.9604	0.9827	0.9763
D23C	0.9524	0.9766	0.9783	0.8543	0.8584	0.8581	0.9637	0.9674	1.0000	0.9863	0.9822	0.9815	0.9891	0.9675	0.9581
D24A	0.9577	0.9835	0.9855	0.8531	0.8583	0.8581	0.9568	0.9569	0.9863	1.0000	0.9948	0.9941	0.9692	0.9493	0.9423
D24B	0.9562	0.9868	0.9861	0.8513	0.8567	0.8615	0.9560	0.9522	0.9822	0.9948	1.0000	0.9984	0.9701	0.9470	0.9410
D24C	0.9538	0.9874	0.9849	0.8496	0.8560	0.8615	0.9551	0.9518	0.9815	0.9941	0.9984	1.0000	0.9700	0.9468	0.9405
D25A	0.9349	0.9600	0.9610	0.8376	0.8406	0.8437	0.9566	0.9604	0.9891	0.9692	0.9701	0.9700	1.0000	0.9686	0.9597
D25B	0.9564	0.9339	0.9345	0.7881	0.7914	0.7931	0.9857	0.9827	0.9675	0.9493	0.9470	0.9468	0.9686	1.0000	0.9886
D25C	0.9522	0.9265	0.9271	0.7768	0.7796	0.7811	0.9935	0.9763	0.9581	0.9423	0.9410	0.9405	0.9597	0.9886	1.0000
Cloth A	0.7893	0.7758	0.7733	0.5764	0.5765	0.5798	0.7951	0.7987	0.7977	0.7797	0.7761	0.7759	0.7973	0.7972	0.7989
Cloth B	0.7850	0.7698	0.7674	0.5692	0.5697	0.5710	0.7904	0.7934	0.7919	0.7726	0.7689	0.7682	0.7930	0.7923	0.7940
Cloth C	0.6637	0.6414	0.6386	0.4451	0.4426	0.4447	0.6735	0.6777	0.6732	0.6304	0.6247	0.6244	0.6836	0.6876	0.6871
Mag A	0.7495	0.7280	0.7274	0.5456	0.5441	0.5454	0.7490	0.7510	0.7505	0.7182	0.7127	0.7119	0.7542	0.7552	0.7550
Mag B	0.4158	0.3855	0.3849	0.2424	0.2385	0.2388	0.4218	0.4194	0.4147	0.3468	0.3436	0.3406	0.4310	0.4375	0.4355
Mag C	0.7393	0.7139	0.7118	0.5277	0.5218	0.5226	0.7376	0.7487	0.7391	0.7091	0.7018	0.7006	0.7391	0.7430	0.7438
Car A	0.0315	0.0033	0.0038	-0.0303	-0.0314	-0.0322	0.0223	0.0161	0.0126	-0.0316	-0.0312	-0.0346	0.0183	0.0242	0.0239
Car B	0.3789	0.3433	0.3432	0.2314	0.2293	0.2296	0.3685	0.3653	0.3627	0.3140	0.3115	0.3090	0.3710	0.3765	0.3758
Car C	0.4156	0.3769	0.3770	0.2746	0.2731	0.2732	0.3924	0.3938	0.3922	0.3618	0.3579	0.3566	0.3944	0.3960	0.3968
B-A Cl	0.6715	0.6450	0.6429	0.5453	0.5389	0.5374	0.6552	0.6683	0.6583	0.6277	0.6195	0.6192	0.6681	0.6699	0.6698
B-B Cl	0.7475	0.7296	0.7279	0.5237	0.5217	0.5235	0.7738	0.7780	0.7769	0.7429	0.7365	0.7365	0.7901	0.7884	0.7908
B-A Mag	0.8681	0.8936	0.8920	0.8842	0.8903	0.8898	0.8247	0.8236	0.8591	0.8594	0.8627	0.8627	0.8548	0.8219	0.8152
B-B Mag	-0.1813	-0.1517	-0.1525	-0.1306	-0.1284	-0.1268	-0.1738	-0.1709	-0.1616	-0.1246	-0.1225	-0.1210	-0.1681	-0.1819	-0.1808
B-A Car	0.8243	0.8226	0.8225	0.7628	0.7624	0.7602	0.7897	0.7963	0.8114	0.7875	0.7818	0.7813	0.8117	0.7944	0.7903
B-B Car	0.0334	0.0535	0.0527	0.0408	0.0418	0.0425	0.0424	0.0450	0.0507	0.0671	0.0665	0.0679	0.0496	0.0430	0.0422

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.7893	0.7850	0.6637	0.7495	0.4158	0.7393	0.0315	0.3789	0.4156	0.6715	0.7475	0.8681	-0.1813	0.8243	0.0334
D21B	0.7758	0.7698	0.6414	0.7280	0.3855	0.7139	0.0033	0.3433	0.3769	0.6450	0.7296	0.8936	-0.1517	0.8226	0.0535
D21C	0.7733	0.7674	0.6386	0.7274	0.3849	0.7118	0.0038	0.3432	0.3770	0.6429	0.7279	0.8920	-0.1525	0.8225	0.0527
D22A	0.5764	0.5692	0.4451	0.5456	0.2424	0.5277	-0.0303	0.2314	0.2746	0.5453	0.5237	0.8842	-0.1306	0.7628	0.0408
D22B	0.5765	0.5697	0.4426	0.5441	0.2385	0.5218	-0.0314	0.2293	0.2731	0.5389	0.5217	0.8903	-0.1284	0.7624	0.0418
D22C	0.5798	0.5710	0.4447	0.5454	0.2388	0.5226	-0.0322	0.2296	0.2732	0.5374	0.5235	0.8898	-0.1268	0.7602	0.0425
D23A	0.7951	0.7904	0.6735	0.7490	0.4218	0.7376	0.0223	0.3685	0.3924	0.6552	0.7738	0.8247	-0.1738	0.7897	0.0424
D23B	0.7987	0.7934	0.6777	0.7510	0.4194	0.7487	0.0161	0.3653	0.3938	0.6683	0.7780	0.8236	-0.1709	0.7963	0.0450
D23C	0.7977	0.7919	0.6732	0.7505	0.4147	0.7391	0.0126	0.3627	0.3922	0.6583	0.7769	0.8591	-0.1616	0.8114	0.0507
D24A	0.7797	0.7726	0.6304	0.7182	0.3468	0.7091	-0.0316	0.3140	0.3618	0.6277	0.7429	0.8594	-0.1246	0.7875	0.0671
D24B	0.7761	0.7689	0.6247	0.7127	0.3436	0.7018	-0.0312	0.3115	0.3579	0.6195	0.7365	0.8627	-0.1225	0.7818	0.0665
D24C	0.7759	0.7682	0.6244	0.7119	0.3406	0.7006	-0.0346	0.3090	0.3566	0.6192	0.7365	0.8627	-0.1210	0.7813	0.0679
D25A	0.7973	0.7930	0.6836	0.7542	0.4310	0.7391	0.0183	0.3710	0.3944	0.6681	0.7901	0.8548	-0.1681	0.8117	0.0496
D25B	0.7972	0.7923	0.6876	0.7552	0.4375	0.7430	0.0242	0.3765	0.3960	0.6699	0.7884	0.8219	-0.1819	0.7944	0.0430
D25C	0.7989	0.7940	0.6871	0.7550	0.4355	0.7438	0.0239	0.3758	0.3968	0.6698	0.7908	0.8152	-0.1808	0.7903	0.0422
Cloth A	1.0000	0.9905	0.9365	0.9476	0.6770	0.9551	0.0929	0.5309	0.5166	0.9058	0.9592	0.8076	-0.2529	0.8677	0.0626
Cloth B	0.9905	1.0000	0.9462	0.9534	0.7033	0.9585	0.1258	0.5521	0.5276	0.9066	0.9596	0.8052	-0.2636	0.8766	0.0503
Cloth C	0.9365	0.9462	1.0000	0.9583	0.8399	0.9539	0.2277	0.6368	0.5618	0.8948	0.9486	0.6743	-0.3270	0.8363	0.0201
Mag A	0.9476	0.9534	0.9583	1.0000	0.8088	0.9540	0.2347	0.6691	0.6247	0.8904	0.9488	0.7502	-0.4138	0.8818	-0.0437
Mag B	0.6770	0.7033	0.8399	0.8088	1.0000	0.7661	0.5096	0.7688	0.5978	0.6492	0.7275	0.4099	-0.4923	0.6542	-0.1488
Mag C	0.9551	0.9585	0.9539	0.9540	0.7661	1.0000	0.1797	0.6041	0.5594	0.9141	0.9430	0.7364	-0.3231	0.8547	0.0179
Car A	0.0929	0.1258	0.2277	0.2347	0.5096	0.1797	1.0000	0.7725	0.6568	0.0686	0.1478	0.0025	-0.4096	0.2726	-0.7770
Car B	0.5309	0.5521	0.6368	0.6691	0.7688	0.6041	0.7725	1.0000	0.8860	0.5061	0.5881	0.3651	-0.5774	0.6307	-0.6018
Car C	0.5166	0.5276	0.5618	0.6247	0.5978	0.5594	0.6568	0.8860	1.0000	0.4948	0.5654	0.4031	-0.5314	0.6049	-0.5234
B-A Cl	0.9058	0.9066	0.8948	0.8904	0.6492	0.9141	0.0686	0.5061	0.4948	1.0000	0.8915	0.7890	-0.2927	0.8852	0.0592
B-B Cl	0.9592	0.9596	0.9486	0.9488	0.7275	0.9430	0.1478	0.5881	0.5654	0.8915	1.0000	0.7365	-0.3423	0.8526	0.0090
B-A Mag	0.8076	0.8052	0.6743	0.7502	0.4099	0.7364	0.0025	0.3651	0.4031	0.7890	0.7365	1.0000	-0.1882	0.9050	0.0523
B-B Mag	-0.2529	-0.2636	-0.3270	-0.4138	-0.4923	-0.3231	-0.4096	-0.5774	-0.5314	-0.2927	-0.3423	-0.1882	1.0000	-0.3538	0.4105
B-A Car	0.8677	0.8766	0.8363	0.8818	0.6542	0.8547	0.2726	0.6307	0.6049	0.8852	0.8526	0.9050	-0.3538	1.0000	-0.1587
B-B Car	0.0626	0.0503	0.0201	-0.0437	-0.1488	0.0179	-0.7770	-0.6018	-0.5234	0.0592	0.0090	0.0523	0.4105	-0.1587	1.0000

Table D.4 PPMC Coefficients for the Indane EIP of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9943	0.9952	0.9416	0.9411	0.9388	0.9911	0.9927	0.9935	0.9926	0.9916	0.9910	0.9863	0.9849	0.9856
D21B	0.9943	1.0000	0.9979	0.9436	0.9410	0.9421	0.9915	0.9874	0.9914	0.9907	0.9928	0.9935	0.9857	0.9836	0.9840
D21C	0.9952	0.9979	1.0000	0.9431	0.9456	0.9456	0.9916	0.9891	0.9918	0.9914	0.9947	0.9949	0.9857	0.9854	0.9843
D22A	0.9416	0.9436	0.9431	1.0000	0.9916	0.9929	0.9313	0.9323	0.9317	0.9321	0.9279	0.9281	0.9252	0.9242	0.9257
D22B	0.9411	0.9410	0.9456	0.9916	1.0000	0.9967	0.9274	0.9296	0.9303	0.9291	0.9300	0.9294	0.9228	0.9226	0.9220
D22C	0.9388	0.9421	0.9456	0.9929	0.9967	1.0000	0.9293	0.9291	0.9298	0.9301	0.9297	0.9297	0.9229	0.9249	0.9243
D23A	0.9911	0.9915	0.9916	0.9313	0.9274	0.9293	1.0000	0.9962	0.9959	0.9949	0.9943	0.9936	0.9950	0.9952	0.9957
D23B	0.9927	0.9874	0.9891	0.9323	0.9296	0.9291	0.9962	1.0000	0.9961	0.9947	0.9925	0.9914	0.9940	0.9944	0.9952
D23C	0.9935	0.9914	0.9918	0.9317	0.9303	0.9298	0.9959	0.9961	1.0000	0.9943	0.9942	0.9934	0.9963	0.9948	0.9951
D24A	0.9926	0.9907	0.9914	0.9321	0.9291	0.9301	0.9949	0.9947	0.9943	1.0000	0.9965	0.9956	0.9896	0.9894	0.9905
D24B	0.9916	0.9928	0.9947	0.9279	0.9300	0.9297	0.9943	0.9925	0.9942	0.9965	1.0000	0.9987	0.9902	0.9899	0.9891
D24C	0.9910	0.9935	0.9949	0.9281	0.9294	0.9297	0.9936	0.9914	0.9934	0.9956	0.9987	1.0000	0.9896	0.9896	0.9885
D25A	0.9863	0.9857	0.9857	0.9252	0.9228	0.9229	0.9950	0.9940	0.9963	0.9896	0.9902	0.9896	1.0000	0.9967	0.9978
D25B	0.9849	0.9836	0.9854	0.9242	0.9226	0.9249	0.9952	0.9944	0.9948	0.9894	0.9899	0.9896	0.9967	1.0000	0.9976
D25C	0.9856	0.9840	0.9843	0.9257	0.9220	0.9243	0.9957	0.9952	0.9951	0.9905	0.9891	0.9885	0.9978	0.9976	1.0000
Cloth A	0.9633	0.9520	0.9565	0.8705	0.8703	0.8670	0.9674	0.9721	0.9654	0.9650	0.9637	0.9589	0.9611	0.9629	0.9639
Cloth B	0.9533	0.9407	0.9463	0.8569	0.8607	0.8582	0.9589	0.9634	0.9569	0.9564	0.9542	0.9477	0.9526	0.9546	0.9569
Cloth C	0.9345	0.9237	0.9274	0.8168	0.8152	0.8137	0.9455	0.9478	0.9427	0.9353	0.9346	0.9286	0.9433	0.9449	0.9457
Mag A	0.9337	0.9203	0.9254	0.8221	0.8238	0.8217	0.9403	0.9437	0.9377	0.9311	0.9296	0.9234	0.9366	0.9381	0.9403
Mag B	0.7951	0.7823	0.7841	0.6513	0.6457	0.6457	0.8160	0.8147	0.8106	0.7862	0.7856	0.7787	0.8233	0.8243	0.8250
Mag C	0.9564	0.9458	0.9500	0.8526	0.8543	0.8523	0.9622	0.9647	0.9604	0.9546	0.9538	0.9483	0.9585	0.9597	0.9613
Car A	0.3442	0.3261	0.3301	0.2384	0.2402	0.2377	0.3523	0.3520	0.3469	0.3176	0.3183	0.3113	0.3550	0.3556	0.3581
Car B	0.8060	0.7914	0.7948	0.6799	0.6782	0.6783	0.8183	0.8193	0.8145	0.7961	0.7944	0.7872	0.8191	0.8222	0.8235
Car C	0.8633	0.8471	0.8519	0.7483	0.7506	0.7483	0.8706	0.8739	0.8681	0.8563	0.8548	0.8482	0.8703	0.8717	0.8737
B-A Cl	0.9557	0.9468	0.9516	0.9004	0.9034	0.9005	0.9578	0.9621	0.9570	0.9538	0.9527	0.9476	0.9536	0.9558	0.9567
B-B Cl	0.9389	0.9306	0.9333	0.8341	0.8316	0.8299	0.9559	0.9572	0.9540	0.9439	0.9444	0.9399	0.9595	0.9603	0.9608
B-A Mag	0.9324	0.9231	0.9303	0.9560	0.9592	0.9556	0.9266	0.9343	0.9262	0.9290	0.9262	0.9208	0.9188	0.9221	0.9230
B-B Mag	0.5165	0.5055	0.5079	0.4170	0.4137	0.4139	0.5261	0.5273	0.5230	0.5030	0.5014	0.4958	0.5302	0.5314	0.5331
B-A Car	0.9562	0.9468	0.9528	0.9323	0.9378	0.9339	0.9559	0.9605	0.9551	0.9493	0.9488	0.9436	0.9525	0.9546	0.9555
B-B Car	-0.0461	-0.0473	-0.0477	-0.0536	-0.0551	-0.0536	-0.0549	-0.0562	-0.0556	-0.0576	-0.0565	-0.0557	-0.0587	-0.0577	-0.0581

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.9633	0.9533	0.9345	0.9337	0.7951	0.9564	0.3442	0.8060	0.8633	0.9557	0.9389	0.9324	0.5165	0.9562	-0.0461
D21B	0.9520	0.9407	0.9237	0.9203	0.7823	0.9458	0.3261	0.7914	0.8471	0.9468	0.9306	0.9231	0.5055	0.9468	-0.0473
D21C	0.9565	0.9463	0.9274	0.9254	0.7841	0.9500	0.3301	0.7948	0.8519	0.9516	0.9333	0.9303	0.5079	0.9528	-0.0477
D22A	0.8705	0.8569	0.8168	0.8221	0.6513	0.8526	0.2384	0.6799	0.7483	0.9004	0.8341	0.9560	0.4170	0.9323	-0.0536
D22B	0.8703	0.8607	0.8152	0.8238	0.6457	0.8543	0.2402	0.6782	0.7506	0.9034	0.8316	0.9592	0.4137	0.9378	-0.0551
D22C	0.8670	0.8582	0.8137	0.8217	0.6457	0.8523	0.2377	0.6783	0.7483	0.9005	0.8299	0.9556	0.4139	0.9339	-0.0536
D23A	0.9674	0.9589	0.9455	0.9403	0.8160	0.9622	0.3523	0.8183	0.8706	0.9578	0.9559	0.9266	0.5261	0.9559	-0.0549
D23B	0.9721	0.9634	0.9478	0.9437	0.8147	0.9647	0.3520	0.8193	0.8739	0.9621	0.9572	0.9343	0.5273	0.9605	-0.0562
D23C	0.9654	0.9569	0.9427	0.9377	0.8106	0.9604	0.3469	0.8145	0.8681	0.9570	0.9540	0.9262	0.5230	0.9551	-0.0556
D24A	0.9650	0.9564	0.9353	0.9311	0.7862	0.9546	0.3176	0.7961	0.8563	0.9538	0.9439	0.9290	0.5030	0.9493	-0.0576
D24B	0.9637	0.9542	0.9346	0.9296	0.7856	0.9538	0.3183	0.7944	0.8548	0.9527	0.9444	0.9262	0.5014	0.9488	-0.0565
D24C	0.9589	0.9477	0.9286	0.9234	0.7787	0.9483	0.3113	0.7872	0.8482	0.9476	0.9399	0.9208	0.4958	0.9436	-0.0557
D25A	0.9611	0.9526	0.9433	0.9366	0.8233	0.9585	0.3550	0.8191	0.8703	0.9536	0.9595	0.9188	0.5302	0.9525	-0.0587
D25B	0.9629	0.9546	0.9449	0.9381	0.8243	0.9597	0.3556	0.8222	0.8717	0.9558	0.9603	0.9221	0.5314	0.9546	-0.0577
D25C	0.9639	0.9569	0.9457	0.9403	0.8250	0.9613	0.3581	0.8235	0.8737	0.9567	0.9608	0.9230	0.5331	0.9555	-0.0581
Cloth A	1.0000	0.9915	0.9843	0.9776	0.8664	0.9883	0.3919	0.8643	0.9141	0.9765	0.9766	0.9241	0.5797	0.9610	-0.0518
Cloth B	0.9915	1.0000	0.9843	0.9800	0.8730	0.9894	0.4117	0.8724	0.9201	0.9757	0.9719	0.9179	0.5836	0.9618	-0.0527
Cloth C	0.9843	0.9843	1.0000	0.9845	0.9236	0.9915	0.4572	0.9027	0.9333	0.9600	0.9814	0.8744	0.6221	0.9387	-0.0455
Mag A	0.9776	0.9800	0.9845	1.0000	0.9199	0.9901	0.4744	0.9090	0.9404	0.9591	0.9753	0.8812	0.6777	0.9436	0.0039
Mag B	0.8664	0.8730	0.9236	0.9199	1.0000	0.9072	0.6122	0.9282	0.9028	0.8327	0.9128	0.7142	0.7216	0.8213	0.0139
Mag C	0.9883	0.9894	0.9915	0.9901	0.9072	1.0000	0.4435	0.8969	0.9342	0.9721	0.9810	0.9002	0.6293	0.9572	-0.0282
Car A	0.3919	0.4117	0.4572	0.4744	0.6122	0.4435	1.0000	0.6875	0.5905	0.3545	0.4488	0.2890	0.5140	0.4018	0.4572
Car B	0.8643	0.8724	0.9027	0.9090	0.9282	0.8969	0.6875	1.0000	0.9356	0.8381	0.8927	0.7437	0.7132	0.8459	0.1980
Car C	0.9141	0.9201	0.9333	0.9404	0.9028	0.9342	0.5905	0.9356	1.0000	0.8940	0.9253	0.8128	0.6794	0.8913	0.1673
B-A Cl	0.9765	0.9757	0.9600	0.9591	0.8327	0.9721	0.3545	0.8381	0.8940	1.0000	0.9574	0.9501	0.5747	0.9793	-0.0415
B-B Cl	0.9766	0.9719	0.9814	0.9753	0.9128	0.9810	0.4488	0.8927	0.9253	0.9574	1.0000	0.8828	0.6417	0.9423	-0.0240
B-A Mag	0.9241	0.9179	0.8744	0.8812	0.7142	0.9002	0.2890	0.7437	0.8128	0.9501	0.8828	1.0000	0.4685	0.9662	-0.0578
B-B Mag	0.5797	0.5836	0.6221	0.6777	0.7216	0.6293	0.5140	0.7132	0.6794	0.5747	0.6417	0.4685	1.0000	0.5679	0.2394
B-A Car	0.9610	0.9618	0.9387	0.9436	0.8213	0.9572	0.4018	0.8459	0.8913	0.9793	0.9423	0.9662	0.5679	1.0000	-0.0033
B-B Car	-0.0518	-0.0527	-0.0455	0.0039	0.0139	-0.0282	0.4572	0.1980	0.1673	-0.0415	-0.0240	-0.0578	0.2394	-0.0033	1.0000

Table D.5 PPMC Coefficients for the OCP EIP of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9923	0.9948	0.9474	0.9348	0.9507	0.9831	0.9739	0.9815	0.9589	0.9593	0.9522	0.9753	0.9783	0.9620
D21B	0.9923	1.0000	0.9971	0.9354	0.9267	0.9404	0.9788	0.9666	0.9804	0.9628	0.9664	0.9623	0.9744	0.9758	0.9609
D21C	0.9948	0.9971	1.0000	0.9383	0.9269	0.9430	0.9825	0.9705	0.9816	0.9674	0.9703	0.9651	0.9741	0.9761	0.9609
D22A	0.9474	0.9354	0.9383	1.0000	0.9798	0.9973	0.9452	0.9368	0.9339	0.8578	0.8579	0.8463	0.9407	0.9453	0.9322
D22B	0.9348	0.9267	0.9269	0.9798	1.0000	0.9791	0.9324	0.9216	0.9463	0.8540	0.8553	0.8445	0.9361	0.9375	0.9243
D22C	0.9507	0.9404	0.9430	0.9973	0.9791	1.0000	0.9474	0.9392	0.9356	0.8634	0.8644	0.8538	0.9436	0.9480	0.9355
D23A	0.9831	0.9788	0.9825	0.9452	0.9324	0.9474	1.0000	0.9831	0.9819	0.9537	0.9555	0.9544	0.9859	0.9878	0.9733
D23B	0.9739	0.9666	0.9705	0.9368	0.9216	0.9392	0.9831	1.0000	0.9682	0.9475	0.9470	0.9449	0.9768	0.9784	0.9629
D23C	0.9815	0.9804	0.9816	0.9339	0.9463	0.9356	0.9819	0.9682	1.0000	0.9591	0.9610	0.9553	0.9812	0.9809	0.9674
D24A	0.9589	0.9628	0.9674	0.8578	0.8540	0.8634	0.9537	0.9475	0.9591	1.0000	0.9963	0.9863	0.9406	0.9395	0.9200
D24B	0.9593	0.9664	0.9703	0.8579	0.8553	0.8644	0.9555	0.9470	0.9610	0.9963	1.0000	0.9906	0.9441	0.9429	0.9224
D24C	0.9522	0.9623	0.9651	0.8463	0.8445	0.8538	0.9544	0.9449	0.9553	0.9863	0.9906	1.0000	0.9462	0.9448	0.9276
D25A	0.9753	0.9744	0.9741	0.9407	0.9361	0.9436	0.9859	0.9768	0.9812	0.9406	0.9441	0.9462	1.0000	0.9946	0.9793
D25B	0.9783	0.9758	0.9761	0.9453	0.9375	0.9480	0.9878	0.9784	0.9809	0.9395	0.9429	0.9448	0.9946	1.0000	0.9828
D25C	0.9620	0.9609	0.9609	0.9322	0.9243	0.9355	0.9733	0.9629	0.9674	0.9200	0.9224	0.9276	0.9793	0.9828	1.0000
Cloth A	0.8447	0.8318	0.8317	0.8438	0.8393	0.8380	0.8472	0.8420	0.8464	0.7932	0.7922	0.7786	0.8527	0.8466	0.8591
Cloth B	0.8338	0.8175	0.8187	0.8531	0.8328	0.8454	0.8368	0.8273	0.8250	0.7601	0.7598	0.7431	0.8359	0.8310	0.8415
Cloth C	0.6933	0.6728	0.6738	0.7548	0.7378	0.7447	0.7139	0.7046	0.7008	0.6008	0.5974	0.5823	0.7116	0.7184	0.7289
Mag A	0.7287	0.7091	0.7038	0.7813	0.7835	0.7761	0.7285	0.7146	0.7314	0.6050	0.6043	0.6014	0.7404	0.7360	0.7502
Mag B	0.6252	0.5947	0.5930	0.7426	0.7174	0.7355	0.6262	0.6084	0.6018	0.4243	0.4256	0.4255	0.6301	0.6318	0.6444
Mag C	0.8216	0.8046	0.8033	0.8724	0.8680	0.8651	0.8265	0.8160	0.8270	0.7179	0.7189	0.7092	0.8305	0.8300	0.8396
Car A	0.2384	0.2079	0.2073	0.3218	0.3024	0.3123	0.2251	0.2064	0.1999	0.0566	0.0577	0.0479	0.2173	0.2213	0.2185
Car B	0.4951	0.4720	0.4659	0.5739	0.5744	0.5680	0.4888	0.4708	0.4820	0.3245	0.3251	0.3267	0.4993	0.4973	0.5074
Car C	0.6317	0.6120	0.6109	0.7119	0.6906	0.7041	0.6387	0.6264	0.6267	0.4943	0.4903	0.4866	0.6326	0.6462	0.6569
B-A Cl	0.7658	0.7506	0.7432	0.8327	0.8397	0.8288	0.7729	0.7629	0.7741	0.6349	0.6336	0.6446	0.7939	0.7946	0.8062
B-B Cl	0.8077	0.7922	0.7867	0.8374	0.8411	0.8326	0.8193	0.8067	0.8225	0.7074	0.7071	0.7033	0.8417	0.8370	0.8485
B-A Mag	0.8684	0.8527	0.8514	0.9261	0.9028	0.9226	0.8725	0.8610	0.8601	0.7532	0.7518	0.7499	0.8736	0.8802	0.8783
B-B Mag	-0.0937	-0.1145	-0.1147	0.0066	-0.0066	-0.0008	-0.1034	-0.1116	-0.1177	-0.2116	-0.2131	-0.2185	-0.1189	-0.1136	-0.1133
B-A Car	0.6822	0.6535	0.6532	0.7758	0.7544	0.7665	0.6822	0.6709	0.6581	0.5123	0.5111	0.4998	0.6822	0.6889	0.6917
B-B Car	-0.1254	-0.1317	-0.1294	-0.1244	-0.1255	-0.1272	-0.1400	-0.1536	-0.1467	-0.1639	-0.1645	-0.1686	-0.1662	-0.1613	-0.1608

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.8447	0.8338	0.6933	0.7287	0.6252	0.8216	0.2384	0.4951	0.6317	0.7658	0.8077	0.8684	-0.0937	0.6822	-0.1254
D21B	0.8318	0.8175	0.6728	0.7091	0.5947	0.8046	0.2079	0.4720	0.6120	0.7506	0.7922	0.8527	-0.1145	0.6535	-0.1317
D21C	0.8317	0.8187	0.6738	0.7038	0.5930	0.8033	0.2073	0.4659	0.6109	0.7432	0.7867	0.8514	-0.1147	0.6532	-0.1294
D22A	0.8438	0.8531	0.7548	0.7813	0.7426	0.8724	0.3218	0.5739	0.7119	0.8327	0.8374	0.9261	0.0066	0.7758	-0.1244
D22B	0.8393	0.8328	0.7378	0.7835	0.7174	0.8680	0.3024	0.5744	0.6906	0.8397	0.8411	0.9028	-0.0066	0.7544	-0.1255
D22C	0.8380	0.8454	0.7447	0.7761	0.7355	0.8651	0.3123	0.5680	0.7041	0.8288	0.8326	0.9226	-0.0008	0.7665	-0.1272
D23A	0.8472	0.8368	0.7139	0.7285	0.6262	0.8265	0.2251	0.4888	0.6387	0.7729	0.8193	0.8725	-0.1034	0.6822	-0.1400
D23B	0.8420	0.8273	0.7046	0.7146	0.6084	0.8160	0.2064	0.4708	0.6264	0.7629	0.8067	0.8610	-0.1116	0.6709	-0.1536
D23C	0.8464	0.8250	0.7008	0.7314	0.6018	0.8270	0.1999	0.4820	0.6267	0.7741	0.8225	0.8601	-0.1177	0.6581	-0.1467
D24A	0.7932	0.7601	0.6008	0.6050	0.4243	0.7179	0.0566	0.3245	0.4943	0.6349	0.7074	0.7532	-0.2116	0.5123	-0.1639
D24B	0.7922	0.7598	0.5974	0.6043	0.4256	0.7189	0.0577	0.3251	0.4903	0.6336	0.7071	0.7518	-0.2131	0.5111	-0.1645
D24C	0.7786	0.7431	0.5823	0.6014	0.4255	0.7092	0.0479	0.3267	0.4866	0.6446	0.7033	0.7499	-0.2185	0.4998	-0.1686
D25A	0.8527	0.8359	0.7116	0.7404	0.6301	0.8305	0.2173	0.4993	0.6326	0.7939	0.8417	0.8736	-0.1189	0.6822	-0.1662
D25B	0.8466	0.8310	0.7184	0.7360	0.6318	0.8300	0.2213	0.4973	0.6462	0.7946	0.8370	0.8802	-0.1136	0.6889	-0.1613
D25C	0.8591	0.8415	0.7289	0.7502	0.6444	0.8396	0.2185	0.5074	0.6569	0.8062	0.8485	0.8783	-0.1133	0.6917	-0.1608
Cloth A	1.0000	0.9765	0.8241	0.8588	0.7035	0.9022	0.3049	0.5990	0.6519	0.8411	0.8967	0.8519	0.0907	0.7833	-0.0742
Cloth B	0.9765	1.0000	0.8375	0.8682	0.7638	0.9126	0.3955	0.6455	0.6930	0.8349	0.8916	0.8612	0.1727	0.8270	-0.0209
Cloth C	0.8241	0.8375	1.0000	0.7614	0.7331	0.8174	0.3675	0.5767	0.8426	0.7495	0.7986	0.7915	0.1941	0.7881	-0.0110
Mag A	0.8588	0.8682	0.7614	1.0000	0.8602	0.8982	0.5577	0.8211	0.7460	0.9375	0.9499	0.8477	0.3686	0.8283	0.0708
Mag B	0.7035	0.7638	0.7331	0.8602	1.0000	0.8417	0.6992	0.8304	0.8030	0.8242	0.8002	0.8127	0.4752	0.8941	0.1532
Mag C	0.9022	0.9126	0.8174	0.8982	0.8417	1.0000	0.4251	0.6850	0.7929	0.8748	0.9038	0.8924	0.2082	0.8053	-0.0061
Car A	0.3049	0.3955	0.3675	0.5577	0.6992	0.4251	1.0000	0.8309	0.5373	0.4570	0.4429	0.3675	0.6672	0.7071	0.5513
Car B	0.5990	0.6455	0.5767	0.8211	0.8304	0.6850	0.8309	1.0000	0.6918	0.7699	0.7418	0.6445	0.5411	0.8341	0.3653
Car C	0.6519	0.6930	0.8426	0.7460	0.8030	0.7929	0.5373	0.6918	1.0000	0.7359	0.7355	0.7732	0.3423	0.7637	0.2476
B-A Cl	0.8411	0.8349	0.7495	0.9375	0.8242	0.8748	0.4570	0.7699	0.7359	1.0000	0.9543	0.9000	0.1676	0.8234	-0.0815
B-B Cl	0.8967	0.8916	0.7986	0.9499	0.8002	0.9038	0.4429	0.7418	0.7355	0.9543	1.0000	0.8964	0.1422	0.8117	-0.0778
B-A Mag	0.8519	0.8612	0.7915	0.8477	0.8127	0.8924	0.3675	0.6445	0.7732	0.9000	0.8964	1.0000	0.0531	0.8251	-0.1076
B-B Mag	0.0907	0.1727	0.1941	0.3686	0.4752	0.2082	0.6672	0.5411	0.3423	0.1676	0.1422	0.0531	1.0000	0.3637	0.5903
B-A Car	0.7833	0.8270	0.7881	0.8283	0.8941	0.8053	0.7071	0.8341	0.7637	0.8234	0.8117	0.8251	0.3637	1.0000	0.2217
B-B Car	-0.0742	-0.0209	-0.0110	0.0708	0.1532	-0.0061	0.5513	0.3653	0.2476	-0.0815	-0.0778	-0.1076	0.5903	0.2217	1.0000

Table D.6 PPMC Coefficients for the PNA EIP of Neat and Burned Diesels (Cloth A-C = Replicates of Burned Diesel 21 from Cloth, Mag A-C = Replicates of Burned Diesel 21 from Magazine, Car A-C = Replicates of Burned Diesel 21 from Carpet, B-A = Blind A, B-B = Blind B, Cl = Cloth, Mag = Magazine, Car = Carpet)

	D21A	D21B	D21C	D22A	D22B	D22C	D23A	D23B	D23C	D24A	D24B	D24C	D25A	D25B	D25C
D21A	1.0000	0.9927	0.9942	0.9503	0.9501	0.9498	0.9825	0.9808	0.9819	0.9886	0.9843	0.9813	0.9716	0.9752	0.9653
D21B	0.9927	1.0000	0.9983	0.9475	0.9467	0.9484	0.9803	0.9760	0.9799	0.9799	0.9896	0.9839	0.9706	0.9727	0.9682
D21C	0.9942	0.9983	1.0000	0.9483	0.9479	0.9491	0.9820	0.9786	0.9811	0.9814	0.9903	0.9849	0.9701	0.9719	0.9670
D22A	0.9503	0.9475	0.9483	1.0000	0.9888	0.9887	0.9286	0.9286	0.9308	0.9399	0.9392	0.9273	0.9374	0.9402	0.9298
D22B	0.9501	0.9467	0.9479	0.9888	1.0000	0.9923	0.9334	0.9296	0.9338	0.9358	0.9320	0.9325	0.9321	0.9347	0.9283
D22C	0.9498	0.9484	0.9491	0.9887	0.9923	1.0000	0.9303	0.9267	0.9315	0.9380	0.9380	0.9300	0.9412	0.9398	0.9348
D23A	0.9825	0.9803	0.9820	0.9286	0.9334	0.9303	1.0000	0.9971	0.9985	0.9802	0.9750	0.9807	0.9757	0.9801	0.9772
D23B	0.9808	0.9760	0.9786	0.9286	0.9296	0.9267	0.9971	1.0000	0.9956	0.9819	0.9739	0.9778	0.9726	0.9775	0.9748
D23C	0.9819	0.9799	0.9811	0.9308	0.9338	0.9315	0.9985	0.9956	1.0000	0.9802	0.9757	0.9792	0.9791	0.9834	0.9795
D24A	0.9886	0.9799	0.9814	0.9399	0.9358	0.9380	0.9802	0.9819	0.9802	1.0000	0.9814	0.9772	0.9743	0.9771	0.9665
D24B	0.9843	0.9896	0.9903	0.9392	0.9320	0.9380	0.9750	0.9739	0.9757	0.9814	1.0000	0.9822	0.9755	0.9737	0.9682
D24C	0.9813	0.9839	0.9849	0.9273	0.9325	0.9300	0.9807	0.9778	0.9792	0.9772	0.9822	1.0000	0.9626	0.9664	0.9703
D25A	0.9716	0.9706	0.9701	0.9374	0.9321	0.9412	0.9757	0.9726	0.9791	0.9743	0.9755	0.9626	1.0000	0.9961	0.9909
D25B	0.9752	0.9727	0.9719	0.9402	0.9347	0.9398	0.9801	0.9775	0.9834	0.9771	0.9737	0.9664	0.9961	1.0000	0.9907
D25C	0.9653	0.9682	0.9670	0.9298	0.9283	0.9348	0.9772	0.9748	0.9795	0.9665	0.9682	0.9703	0.9909	0.9907	1.0000
Cloth A	0.7254	0.7027	0.7092	0.7086	0.7239	0.7011	0.7174	0.7276	0.7100	0.7125	0.6833	0.7044	0.6734	0.6831	0.6843
Cloth B	0.7892	0.7732	0.7804	0.7590	0.7555	0.7358	0.7850	0.8024	0.7776	0.7799	0.7640	0.7754	0.7446	0.7543	0.7606
Cloth C	0.7745	0.7506	0.7566	0.7261	0.7394	0.7186	0.7734	0.7846	0.7663	0.7604	0.7295	0.7543	0.7387	0.7487	0.7553
Mag A	0.7623	0.7526	0.7566	0.7755	0.7794	0.7837	0.7487	0.7522	0.7492	0.7502	0.7498	0.7495	0.7775	0.7731	0.7752
Mag B	0.7812	0.7728	0.7747	0.7584	0.7524	0.7643	0.7542	0.7497	0.7533	0.7526	0.7574	0.7461	0.8066	0.7989	0.7938
Mag C	0.8654	0.8532	0.8568	0.8186	0.8106	0.8170	0.8376	0.8428	0.8374	0.8471	0.8507	0.8339	0.8775	0.8716	0.8683
Car A	0.4997	0.4851	0.4857	0.4109	0.4165	0.4081	0.4936	0.4840	0.4877	0.4584	0.4543	0.4635	0.4916	0.4930	0.4976
Car B	0.8782	0.8665	0.8672	0.8355	0.8268	0.8325	0.8651	0.8647	0.8647	0.8629	0.8562	0.8432	0.8974	0.8940	0.8906
Car C	0.8054	0.7832	0.7892	0.7455	0.7575	0.7389	0.8011	0.8109	0.7946	0.7806	0.7593	0.7802	0.7673	0.7792	0.7847
B-A Cl	0.7299	0.7209	0.7263	0.7652	0.7575	0.7630	0.6913	0.6958	0.6895	0.7121	0.7138	0.7059	0.7391	0.7268	0.7293
B-B Cl	0.8303	0.8297	0.8309	0.8425	0.8304	0.8493	0.8153	0.8142	0.8165	0.8296	0.8315	0.8125	0.8706	0.8600	0.8520
B-A Mag	0.7161	0.7086	0.7136	0.7479	0.7445	0.7498	0.6697	0.6741	0.6678	0.6949	0.7011	0.6924	0.7172	0.7063	0.7083
B-B Mag	0.7433	0.7349	0.7353	0.7006	0.6996	0.7084	0.7525	0.7573	0.7565	0.7395	0.7391	0.7332	0.7907	0.7899	0.7893
B-A Car	0.8910	0.8763	0.8784	0.9044	0.9100	0.9126	0.8741	0.8789	0.8732	0.8806	0.8647	0.8616	0.8960	0.8954	0.8976
B-B Car	0.2500	0.2529	0.2516	0.2388	0.2292	0.2346	0.2618	0.2566	0.2620	0.2550	0.2563	0.2485	0.2767	0.2753	0.2726

	Cloth A	Cloth B	Cloth C	Mag A	Mag B	Mag C	Car A	Car B	Car C	B-A Cl	B-B Cl	B-A Mag	B-B Mag	B-A Car	B-B Car
D21A	0.7254	0.7892	0.7745	0.7623	0.7812	0.8654	0.4997	0.8782	0.8054	0.7299	0.8303	0.7161	0.7433	0.8910	0.2500
D21B	0.7027	0.7732	0.7506	0.7526	0.7728	0.8532	0.4851	0.8665	0.7832	0.7209	0.8297	0.7086	0.7349	0.8763	0.2529
D21C	0.7092	0.7804	0.7566	0.7566	0.7747	0.8568	0.4857	0.8672	0.7892	0.7263	0.8309	0.7136	0.7353	0.8784	0.2516
D22A	0.7086	0.7590	0.7261	0.7755	0.7584	0.8186	0.4109	0.8355	0.7455	0.7652	0.8425	0.7479	0.7006	0.9044	0.2388
D22B	0.7239	0.7555	0.7394	0.7794	0.7524	0.8106	0.4165	0.8268	0.7575	0.7575	0.8304	0.7445	0.6996	0.9100	0.2292
D22C	0.7011	0.7358	0.7186	0.7837	0.7643	0.8170	0.4081	0.8325	0.7389	0.7630	0.8493	0.7498	0.7084	0.9126	0.2346
D23A	0.7174	0.7850	0.7734	0.7487	0.7542	0.8376	0.4936	0.8651	0.8011	0.6913	0.8153	0.6697	0.7525	0.8741	0.2618
D23B	0.7276	0.8024	0.7846	0.7522	0.7497	0.8428	0.4840	0.8647	0.8109	0.6958	0.8142	0.6741	0.7573	0.8789	0.2566
D23C	0.7100	0.7776	0.7663	0.7492	0.7533	0.8374	0.4877	0.8647	0.7946	0.6895	0.8165	0.6678	0.7565	0.8732	0.2620
D24A	0.7125	0.7799	0.7604	0.7502	0.7526	0.8471	0.4584	0.8629	0.7806	0.7121	0.8296	0.6949	0.7395	0.8806	0.2550
D24B	0.6833	0.7640	0.7295	0.7498	0.7574	0.8507	0.4543	0.8562	0.7593	0.7138	0.8315	0.7011	0.7391	0.8647	0.2563
D24C	0.7044	0.7754	0.7543	0.7495	0.7461	0.8339	0.4635	0.8432	0.7802	0.7059	0.8125	0.6924	0.7332	0.8616	0.2485
D25A	0.6734	0.7446	0.7387	0.7775	0.8066	0.8775	0.4916	0.8974	0.7673	0.7391	0.8706	0.7172	0.7907	0.8960	0.2767
D25B	0.6831	0.7543	0.7487	0.7731	0.7989	0.8716	0.4930	0.8940	0.7792	0.7268	0.8600	0.7063	0.7899	0.8954	0.2753
D25C	0.6843	0.7606	0.7553	0.7752	0.7938	0.8683	0.4976	0.8906	0.7847	0.7293	0.8520	0.7083	0.7893	0.8976	0.2726
Cloth A	1.0000	0.9412	0.9522	0.8098	0.6420	0.7574	0.4674	0.6944	0.8962	0.7698	0.6376	0.7523	0.6231	0.7756	0.1493
Cloth B	0.9412	1.0000	0.9544	0.8209	0.6759	0.8386	0.5125	0.7539	0.9298	0.8007	0.6731	0.7935	0.6821	0.8025	0.1740
Cloth C	0.9522	0.9544	1.0000	0.8045	0.7157	0.8261	0.5632	0.7749	0.9414	0.7851	0.6784	0.7671	0.6868	0.8377	0.1716
Mag A	0.8098	0.8209	0.8045	1.0000	0.7959	0.8827	0.4761	0.7649	0.8156	0.8894	0.8088	0.8733	0.8160	0.7846	0.2233
Mag B	0.6420	0.6759	0.7157	0.7959	1.0000	0.8709	0.6147	0.8668	0.7561	0.8440	0.9253	0.7989	0.7657	0.8185	0.2463
Mag C	0.7574	0.8386	0.8261	0.8827	0.8709	1.0000	0.5774	0.8753	0.8680	0.8875	0.8521	0.8942	0.8424	0.8398	0.2355
Car A	0.4674	0.5125	0.5632	0.4761	0.6147	0.5774	1.0000	0.6788	0.6073	0.4518	0.4318	0.4401	0.4711	0.5032	0.4503
Car B	0.6944	0.7539	0.7749	0.7649	0.8668	0.8753	0.6788	1.0000	0.8173	0.7469	0.8302	0.7040	0.7818	0.8817	0.3949
Car C	0.8962	0.9298	0.9414	0.8156	0.7561	0.8680	0.6073	0.8173	1.0000	0.7689	0.6942	0.7711	0.7408	0.8291	0.2310
B-A Cl	0.7698	0.8007	0.7851	0.8894	0.8440	0.8875	0.4518	0.7469	0.7689	1.0000	0.8738	0.9679	0.7200	0.7942	0.1807
B-B Cl	0.6376	0.6731	0.6784	0.8088	0.9253	0.8521	0.4318	0.8302	0.6942	0.8738	1.0000	0.8231	0.7671	0.8465	0.2466
B-A Mag	0.7523	0.7935	0.7671	0.8733	0.7989	0.8942	0.4401	0.7040	0.7711	0.9679	0.8231	1.0000	0.6989	0.7561	0.1712
B-B Mag	0.6231	0.6821	0.6868	0.8160	0.7657	0.8424	0.4711	0.7818	0.7408	0.7200	0.7671	0.6989	1.0000	0.7391	0.2453
B-A Car	0.7756	0.8025	0.8377	0.7846	0.8185	0.8398	0.5032	0.8817	0.8291	0.7942	0.8465	0.7561	0.7391	1.0000	0.2429
B-B Car	0.1493	0.1740	0.1716	0.2233	0.2463	0.2355	0.4503	0.3949	0.2310	0.1807	0.2466	0.1712	0.2453	0.2429	1.0000

References

[1] Saferstein, R. *Criminalistics: An Introduction to Forensic Science*, 9th ed. Upper Saddle River, NJ: Prentice Hall, **2006**.

[2] http://www.usfa.dhs.gov/statistics/arson/index.shtm.

[3] http://www.fbi.gov/ucr/cius_02/html/web/offreported/02-narson11.html.

[4] American Society for Testing and Materials, ASTM E1618-06e1. *Annual Book of ASTM Standards 14.02.*

[5] American Society for Testing and Materials, ASTM E1387-01. *Annual Book of ASTM Standards 14.02.*

[6] http://www.astm.org/COMMIT/COMMITTEE/E30.htm.

[7] American Society for Testing and Materials, ASTM E1385-00. *Annual Book of ASTM Standards 14.02.*

[8] American Society for Testing and Materials, ASTM E1386-00(2005). *Annual Book of ASTM Standards 14.02.*

[9] American Society for Testing and Materials, ASTM E1412-07. *Annual Book of ASTM Standards 14.02.*

[10] American Society for Testing and Materials, ASTM E1413-07. *Annual Book of ASTM Standards 14.02.*

[11] American Society for Testing and Materials, ASTM E2154-01. *Annual Book of ASTM Standards 14.02.*

[12] Smith, R.M. *Analytical Chemistry* **1982**, *54*, 1399A-1409A.

[13] Mann, D.C. *Journal of Forensic Sciences* **1987**, *32*, 606-628.

[14] Barnes, A.T.; Dolan, J.A.; Kuk, R.J.; Siegel, J.A. *Journal of Forensic Sciences* **2004**, *49*, 1018-1023.

[15] Sigman, M.E.; Williams, M.R.; Ivy, R.G. *Analytical Chemistry* **2007**, *79*, 3462-3468.

[16] Sandercock, P.M.L.; Du Pasquier, E. *Forensic Science International* **2003**, *134*, 1-10.

[17] Sandercock, P.M.L.; Du Pasquier, E. *Forensic Science International* **2004**, *140*, 71-77.

[18] Sandercock, P.M.L.; Du Pasquier, E. *Forensic Science International* **2004**, *140*, 43-59.

[19] Tan B.; Hardy, J.K.; Snavely, R.E. *Analytica Chimica Acta* **2000**, *422*, 37-46.

[20] Doble, P.; Sandercock, M.; Du Pasquier, E.; Petocz, P.; Roux, C.; Dawson, M. *Forensic Science International* **2003**, *132*, 26-39.

[21] Wang, Z.; Yang, C.; Fingas, M.; Hollebone, B.; Peng, X.; Hansen, A.B.; Christensen, J.H. *Environmental Science & Technology* **2005**, *39*, 8700-8707.

[22] Wang, Z.; Yang, C.; Hollebone, B.;Fingas, M. *Environmental Science & Technology* **2006**, *40*, 5636-5646.

[23] Gaines, R.B.; Hall, G.J.; Frysinger, G.S.; Gronlund, W.R.; Juaire, K.L. *Environmental Forensics* **2006**, *7*, 77-87.

[24] Gaines, R.B.; Frysinger, G.S.; Hendrick-Smith, M.S.; Stuart, J.D. *Environmental Science & Technology* **1999**, *33*, 2106-2112.

[25] Wang, F.C.; Qian, K.; Green, L.A. *Analytical Chemistry* **2005**, *77*, 2777-2785.

[26] Johnson, K.J.; Wright, B.W.; Jarman, K.H.; Synovec, R.E. *Journal of Chromatography A* **2003**, *996*, 141-155.

[27] Brereton, R.G. *Applied Chemometrics for Scientists*. Hoboken, NJ: John Wiley & Sons, Ltd, **2007**.

[28] Bertsch, W. *Journal of Chromatography A* **1994**, *674*, 329-333.

[29] Cavanagh, K.; Du Pasquier, E.; Lennard, C. *Forensic Science International* **2002**, *125*, 22-36.

[30] Lentini, J.L.; Dolan, J.A.; Cherry, C. *Journal of Forensic Sciences* **2000**, *45*, 968-989.

[31] Almirall, J.R.; Furton, K.G. *Journal of Analytical and Applied Pyrolysis* **2004**, *71*, 51-67.

[32] Borusiewicz, R.; Zieba-Palus, J.; Zadora, G. *Forensic Science International* **2006**, *160*, 115-126.

[33] Hupp, A.M.; Marshall, L.J.; Campbell, D.I.; Smith, R.W.; McGuffin, V.L. *Analytica Chimica Acta* **2008**, *606*, 159-171.

[34] Devore, J.L. *Probability and Statistics for Engineering and the Sciences*, 4th ed. Belmont, CA: Duxbury Press, **1995**.

[35] Smith, L.I. *A tutorial on Principal Components Analysis.* http://www.seas.harvard.edu/courses/cs171/lectures/principal_components.pdf, **2002**.

[36] Freudenrich, C.C. *Science Channel: How Stuff Works.* http://science.howstuffworks.com/oil-refining.htm.

[37] "Advanced Fire Debris Analysis Workshop." Presented by FBI Laboratory Explosives Unit. Indianapolis, IN, April 15-17, 2008.

[38] Skoog, D.A.; Holler, F.J.; Crouch, S.R. *Principles of Instrumental Analysis*, 6th ed. Belmont, CA: Thomson, **2007**.

[39] "Advanced Fire Debris Analysis Workshop." Presented by Midwestern Association of Forensic Scientists. Traverse City, MI, September 24. 2007.

[40] *Ignitable Liquid Reference Collection.* http://www.ncfs.org/ilrc1.html.

[41] Nielsen, N.V.; Carstensen, J.M.; Smedsgaard, J. *Journal of Chromatography A* **1998**, *805*, 17-35.

[42] Tomasi, G.; van den Berg, F.; Andersson, C. *Journal of Chemometrics* **2004**, *18*, 231-241.

[43] van Nederkassel, A.M.; Daszykowski, M.; Eilers, P.H.C.; Vander Heyden, Y. *Journal of Chromatography A* **2006**, *1118*, 199-210.

[44] Pierce, K.M.; Hope, J.L.; Johnson, K.J., Wright, B.W.; Synovec, R.E. *Journal of Chromatography A* **2005**, *1096*, 101-110.