



# A foundational study of fire debris interpretation using quantitative measures of chromatographic features in gasoline and the use of graphical display to demonstrate data sufficiency

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## ABSTRACT

The analytical process for identifying ignitable liquids is based on fundamental chemical properties; however, the current interpretation of these properties as chromatographic data relies on subjective pattern recognition techniques. The subjectivity of these pattern recognition techniques increases with the presence of complex matrix contribution. To make the fire debris interpretation process more standardized and objective, a novel method is proposed for analyzing fire debris Gas Chromatography-Mass Spectrometry (GC-MS) data using quantitative measures of chromatographic features of interest. These features are represented by peak height ratios observed in the Total Ion Chromatograph and Extracted Ion Profiles.

Chromatographic features of interest in 150 gasoline samples were evaluated and 64 chromatographic peak height ratios were selected for study. Statistical analysis was conducted to determine the variation observed for each of these ratios in the gasoline samples and to determine the frequency of these features in negative matrix samples. This information was evaluated to determine relative significance, as represented by the assigned points for each of these features. When summed and used as plot values, these cumulative scores graphically display the separation of gasoline samples from negative matrix samples using this methodology. The scores were used to create a sufficiency graph, which is a graphical display detailing the totality of data supporting a potential gasoline identification. The sufficiency graph also identifies the “gray” area where analysts are more likely to form differing opinions.

The methodologies introduced are a step toward a documentation process that ensures greater transparency in fire debris examinations and comparisons. The methods generate a quantitative sufficiency graph for consistent data interpretation and documentation.

## 1. Introduction

### 1.1. Subjectivity in ignitable liquid analysis

The 2009 NAS report, Strengthening Forensic Science in the United States: A Path Forward, dictates the need to develop rigorous protocols for performing subjective interpretations [1]. This report was particularly critical of pattern matching disciplines such as friction ridge analysis, firearms analysis, and impressions comparisons. However, some chemistry disciplines of forensic science also involve pattern matching. Forensic analysis of fire debris for the presence of ignitable liquids is a chromatographic pattern recognition process that, for

complex samples, can have a high degree of subjectivity. While there is literature that describes the basic chromatographic pattern characteristics of various ignitable liquid classes [2–4], and there is some literature for processes that apply statistical methods to identify and/or differentiate ignitable liquids [5–8], there is no published or peer-reviewed literature that applies statistical modeling in a way that directly translates to the visual pattern recognition techniques currently employed in the field. Furthermore, there is a lack of data detailing the variability of peak presentations within these visual pattern markers in either the presence or absence of matrix contributions.

“ASTM E1618-19: Standard Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography Mass

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Spectrometry [4] provides general criteria that describes each class of ignitable liquid, but does not provide sufficient criteria for chromatographic pattern comparisons of Total Ion Chromatograms (TICs) or Extracted Ion Profiles (EIPs) when determining if an ignitable liquid is present in a forensic sample. These comparisons can be complicated by the introduction of sample variables such as matrix contributions, degradation, or sample evaporation, which commonly result in complex chromatographic patterns from the evidentiary samples. The comparisons of complex sample patterns to reference ignitable liquids require a high degree of subjective interpretation where results can vary based on the perspective of the examiner.

The published studies and standards for ignitable liquid analysis by Gas Chromatography-Mass Spectrometry (GC-MS) are primarily focused on neat liquid analysis [9,10]. The identification and classification of an unknown neat ignitable liquid is generally straightforward. Chromatographic peak patterns from the TIC and EIPs representing the hydrocarbon classes most commonly found in petroleum products (alkylbenzenes, alkanes/isoalkanes, indanes, polynuclear aromatics, and cycloalkanes) from the forensic sample are compared to those of reference ignitable liquids. Further complicating interpretation, many of the hydrocarbon compounds found in petroleum products are also found in the matrices from which they are extracted [11–14]. The analyst is tasked with determining if the compounds and associated peak patterns presented by the data are due to an ignitable liquid or are a result of pyrolysis of synthetic materials or other matrix contributions. Previous studies associated with the comparison of reference ignitable liquids to forensic samples were generally based upon visual subjective comparison techniques [9,15], instrumental techniques not commonly utilized in forensic laboratories [16–19], or statistical methods that do not use the current standardized methodology [20–22].

This study was designed to develop and validate a more objective data interpretation process for the identification of ignitable liquids. The focus of this foundational study was the identification of gasoline. Gasoline is composed of hundreds of individual compounds that form distinct patterns in the TIC and EIPs. The large number of individual compounds produce many chromatographic features of interest. This project does not require that a select number of specific compounds merely be present to identify gasoline, but rather examines the chromatographic features of interest present throughout the entirety of the data, as presented by presence and peak height ratio, and categorically ranks them by the support they provide to the identification of gasoline. This establishes a novel, validated methodology to quantitatively assess the chromatographic features of gasoline in comparison to complex matrix samples through the application of statistical measures. This methodology reduces the subjectivity in the data interpretation process of complex samples and could be applied to an overall decision-making process.

The first step in this process was to objectively determine identifying criteria for gasoline. Gasoline is created by blending various petroleum refinery fractions [23,24]. Within a refinery fraction, the hydrocarbon compositions, including relative concentrations, tend to be consistent. Variation comes primarily from the blending process. The selection of refinery processes used to produce the fractions and the quantities of each fraction included in the blend can result in nuanced differences among various gasoline samples [25–27].

The goal of this process was to determine chromatographic criteria that would be present and consistent among a variety of gasoline samples collected from multiple sources and geographic locations at various evaporation levels and that could be distinguished using various chromatographic analysis methods. The significance of each of these criteria with respect to matrix contribution was determined. While this is the basis of current methodology, including those stated in ASTM E1618 [4], there have not been published studies addressing the nuanced variability of composition and chromatographic features.

## 1.2. Overview and application of the friction ridge sufficiency graph

When complex samples are involved, the relatively subjective pattern matching technique used for both friction ridge analysis and ignitable liquid analysis could result in examiners reaching different conclusions. The approaches used by latent print examiners to reduce the subjectivity of analysis and increase the transparency of documentation are applied to ignitable liquid analysis in this study to obtain a similar outcome.

The first analysis step used by the friction ridge analysis discipline toward this effort is to determine the value of the pattern based on the details that are present [28,29]. This value is then used to determine the suitability of the evidentiary patterns for comparison. To visually represent the relationship between the quality and quantity of the data present for interpretation in friction ridge analysis, the Scientific Working Group on Friction Ridge Analysis, Study and Technology (SWGFAST) developed a sufficiency graph with two decision lines, one solid and one dotted, that delineate three reference regions: A, B, and C (Fig. 1) [30]. The solid curve defines the lower limit of sufficiency below which the information available to make a conclusion is insufficient and further review or analysis is not warranted (Region A). The dotted upper curve indicates the boundary between complex and non-complex samples (Regions B and C). In the area in-between the solid line and dotted line, the examination is considered complex and further analysis or review with enhanced documentation may be warranted (Region B). In the area above the dotted line, the examination is considered non-complex and a determination should be deemed conclusive (Region C). The complex region, B, is where varied conclusions may be reached. Research within the friction ridge analysis discipline showed that disagreements in conclusions were most prevalent in this complex region (Region B) and were generally a product of different examiners' judgement that there was enough information to make a conclusion [28].

The friction ridge sufficiency graph is useful for discussing comparisons between examiners and for displaying the level of complexity of the comparison [28]. However, it was generated as a theoretical, qualitative model based on the collective experience of members of SWGFAST, and not on the basis of quantitative data.

A graph similar to the Friction Ridge Sufficiency Graph has the potential to depict the continuum of data encountered in ignitable liquid analysis. For application to the field of ignitable liquid analysis, a data-based, quantitative approach is used in this study to determine and optimize decision line shapes and placements and to define the regions of data sufficiency.

For ignitable liquid analysis the “quality” and “quantity” of the data is represented by the amount of supporting data present in the TIC and the EIPs. The data in the TIC is most affected by the presence of a complex matrix. This matrix contribution can mask data supportive of a conclusion and can contribute to the abundance of some compounds

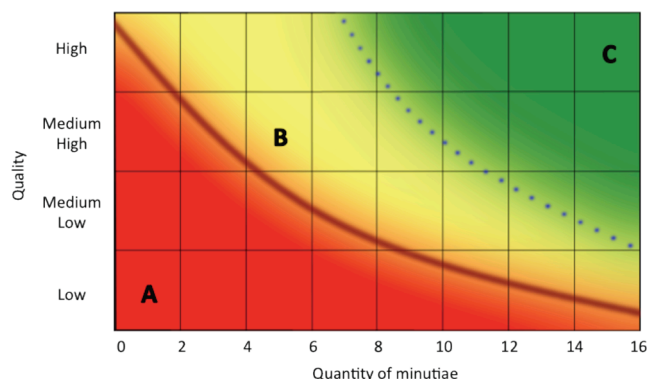


Fig. 1. Friction ridge sufficiency graph.

found in ignitable liquids and the matrix. EIPs extract the ions of interest for a class of compounds that represent ignitable liquids. These extracted profiles are generally less affected by matrix contribution. Using a points system developed as a part of this study, known data sets, including gasoline samples, negative matrix samples, and samples of matrix spiked with gasoline were plotted on the graph. These data sets were used to establish decision lines that are statistically placed and separate the data regions similarly to the friction ridge sufficiency graph. This sufficiency graph with the decision lines identifies an area where high difficulty data will fall, which is the area where examiners may be more likely to differ in conclusions. Once established for gasoline, the sufficiency graph was validated using unknown complex samples, known ignitable liquid samples from other classifications, and samples analyzed by chromatographic methods from additional forensic laboratories.

The quantitative interpretation method, including the sufficiency graph, are introduced as a mechanism to identify and reduce the potential for error. Critics of the methodology used in friction ridge analysis agree that “greater visibility of the experts’ inferential process would be of value both when reaching and verifying a fingerprint decision, and when explaining that decision to a court of lay individuals” [28]. This method generates a quantitative sufficiency chart to make the fire debris experts’ inferential process standardized with the use of a validated method and objective by using quantitative measures.

## 2. Material and methods

### 2.1. Selection of chromatographic features for analysis

Traditional data analysis includes the separation and identification of individual compounds by GC–MS and the comparison of relative peak ratios of closely eluting compounds in the TIC and EIPs. When analyzing fire debris for the presence of ignitable liquids, ions indicative of a hydrocarbon class are extracted and summed to create extracted ion profiles [2,3,26,31]. The selection of compounds and extracted ion profiles for use in this study (Table 1) was based upon the following considerations:

- Relative abundance in TIC and/or EIP data, to include major compounds
- Resolution in TIC and/or EIP data, such that the peak apex could be distinguished
- Representation of hydrocarbon classes
- Boiling point range with consideration given to evaporation levels

The majority of the aromatic, indane and polynuclear aromatic compounds selected are well represented in the current literature [3,4,32,33]. The aromatic and indane chromatographic features were expanded somewhat from those in the literature to include a broader

range of compounds. The selected aromatic compounds in the TIC and EIP include additional C4 alkylbenzenes and C5 alkylbenzenes. The selected indane compounds in the TIC and EIP include additional, larger molecular weight indane compounds.

The selected alkane compounds from the TIC were limited to resolved compounds of sufficient abundance that were present in multiple evaporation levels, this excluded the aliphatic compounds that elute before n-C8 (octane). The alkane compounds included in the alkane/isoalkane profile were further limited to those that elute between n-C10 (decane) and n-C12 (dodecane). This region includes peaks/patterns associated with medium isoparaffinic products. Iso-paraffinic refinery fractions are added to gasoline to increase the octane ratings [26,31,34].

Chromatographic features of interest are labeled in representative data from a single gasoline source (Figs. 2–6). The nomenclature used in Figs. 2–6 includes an alphanumeric designation. In cases where the number of isomers preclude a known composition, letters or numbers were used to denote the peak. For example, C4 alkylbenzenes are known components of gasoline, however, the exact elution of each of the C4 alkylbenzene isomers has not been determined. In the representative data, each of the peak names in a gray box were eliminated from study when the statistical analysis of these peaks did not meet the study objectives or because the peak did not elute near a compound of the same class. The nomenclature is also described in Table 2.

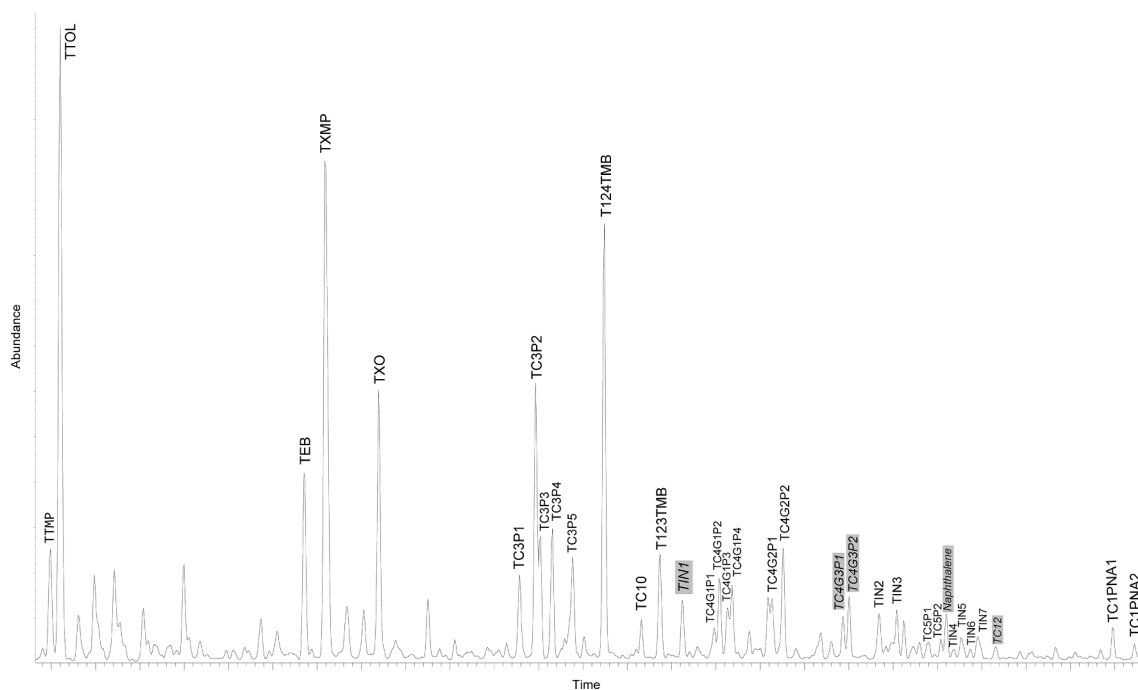
### 2.2. Gasoline samples

A gasoline control database was created by analyzing  $n = 30$  gasoline samples collected from three geographic regions (Eastern Virginia, Western Florida, and Central Louisiana). An aliquot of each gasoline sample was then evaporated by volume to four levels (25%, 50%, 75%, and 90%), resulting in  $n = 150$  samples. Each sample was analyzed at three different laboratories (Virginia Department of Forensic Science - Norfolk, Pinellas County Forensic Lab - Florida, and Louisiana State Police - Baton Rouge) as a solvent dilution with the instrumental conditions that each laboratory used for casework (Table 3). The instrumental methods included two HP-1 Gas Chromatography (GC) columns with different temperature and flow parameters and one HP-5 GC column. Although the different instrument conditions resulted in slightly different chromatography, care was taken to select the same compound for each evaluation from all resulting data by comparing the mass spectrum of the compounds. The resultant gasoline control database contained  $n = 450$  gasoline data files.

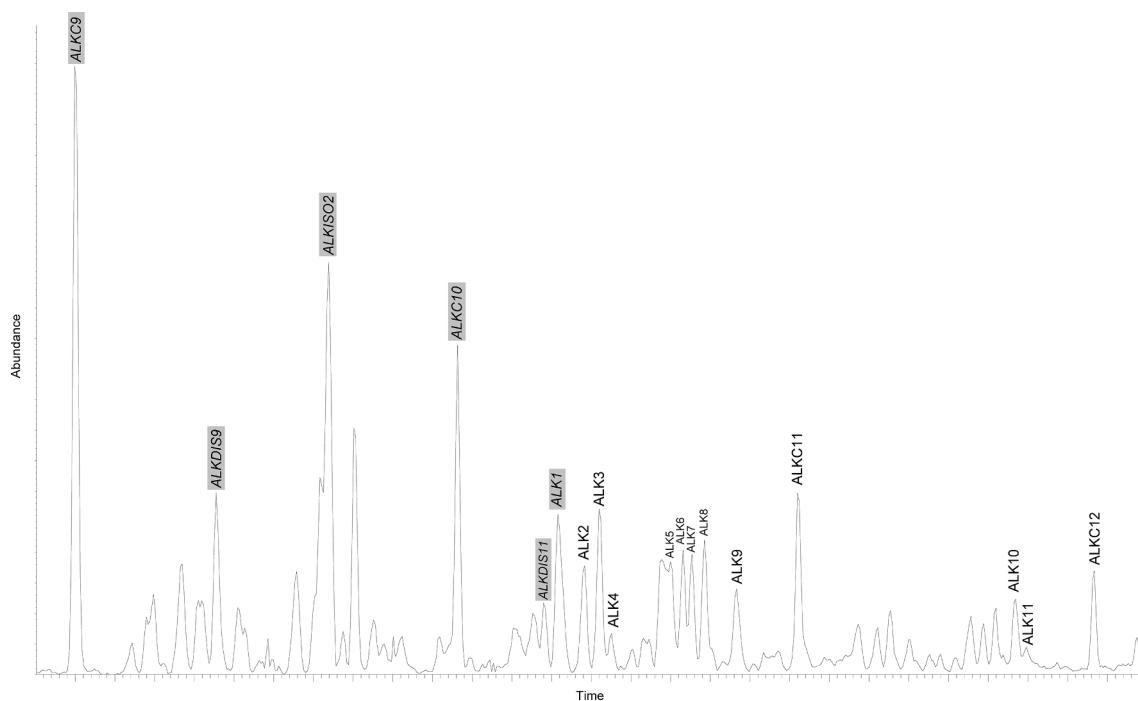
The gasoline sample data files were processed by collecting the individual peak heights of the chromatographic features of interest. The peak heights were then used in ratio pairs of closely eluting compounds within a given sample. Peak height ratios of closely eluting peaks (peak pairs) were determined to be analogous to the visual pattern recognition

**Table 1**  
Chromatographic features of interest in the TIC and each of the EIPs.

Data Display	Ions ( $m/z$ )	Final Number of Collected Peak Heights	Final Number of Ratios Calculated	Compounds of Interest
TIC	All Tabulated	34	21	2,3,4-trimethylpentane, toluene, ethylbenzene, xylenes (M,P,O), C3 alkylbenzenes, 1,2,4-trimethylbenzene, decane, 1,2,3-trimethylbenzene, indane, C4 alkylbenzenes, indanes and indenenes, C5 alkylbenzenes, naphthalene, dodecane, 1-methylnaphthalene, 2-methylnaphthalene
Alkane/isoalkane EIP	57, 71, 85, 99	14	8	Normal alkanes within the medium boiling range (n-C10 to n-C12) and prominent branched alkanes that represent the isoparaffinic and distillate fraction with the n-C10 to n-C12 range
Aromatic/alkylbenzene EIP	91, 105, 119, 133	25	15	Toluene, ethylbenzene, xylenes (M,P,O), C3 alkylbenzenes, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, C4 alkylbenzenes, C5 alkylbenzenes
Indane EIP	117, 118, 131, 132	11	6	Indane and indene compounds that form the prominent peaks within the profile
Polynuclear aromatic EIP	128, 142, 156	3	1	Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene



**Fig. 2.** A representative total ion chromatogram of a 50% evaporated gasoline sample. Peaks used in assessing peak pair ratios were labeled with their designated peak code, where T = TIC, followed by letters or numbers representing either the known composition of the peak, or in cases where the number of isomers preclude a known composition, letters or numbers to denote the peak. Grayed labels indicate peaks that did not meet study objectives of statistical significance or did not elute near a similar compound to be included in a ratio.

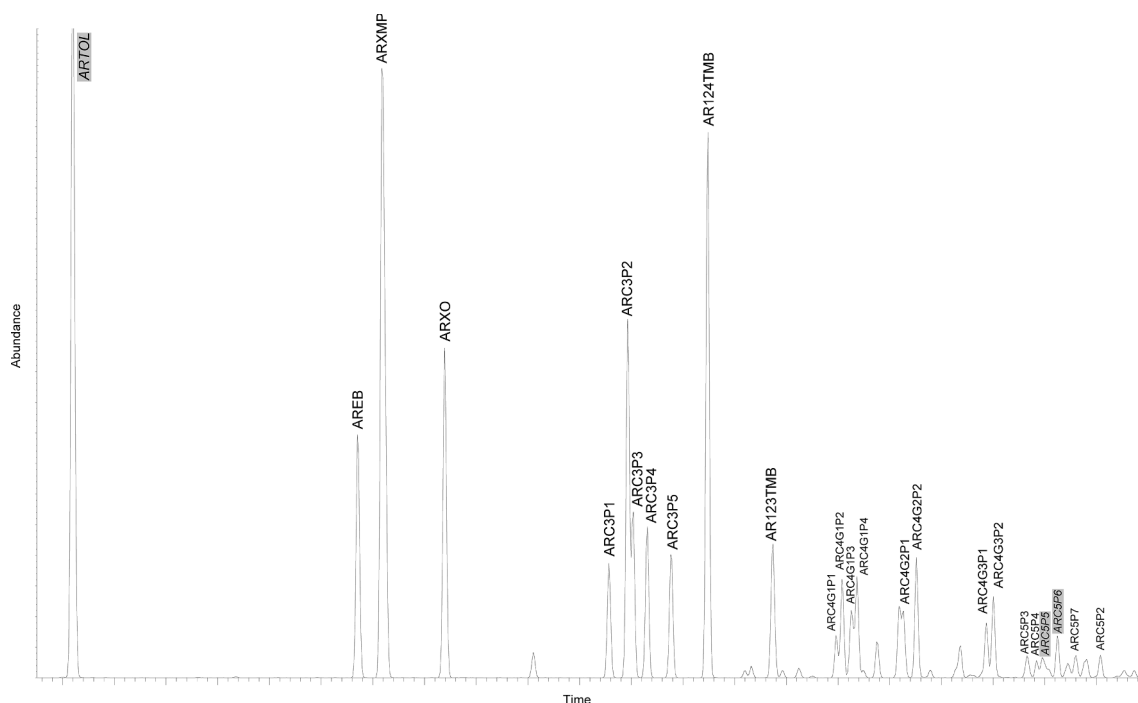


**Fig. 3.** A representative alkane/isoalkane extracted ion profile of a 50% evaporated gasoline sample. Peaks used in assessing peak pair ratios were labeled with their designated peak code, where ALK = alkane/isoalkane profile, followed by letters or numbers representing either the known composition of the peak, or in cases where the number of isomers preclude a known composition, letters or numbers to denote the peak. Grayed labels indicate peaks that did not meet study objectives of statistical significance or did not elute near a similar compound to be included in a ratio.

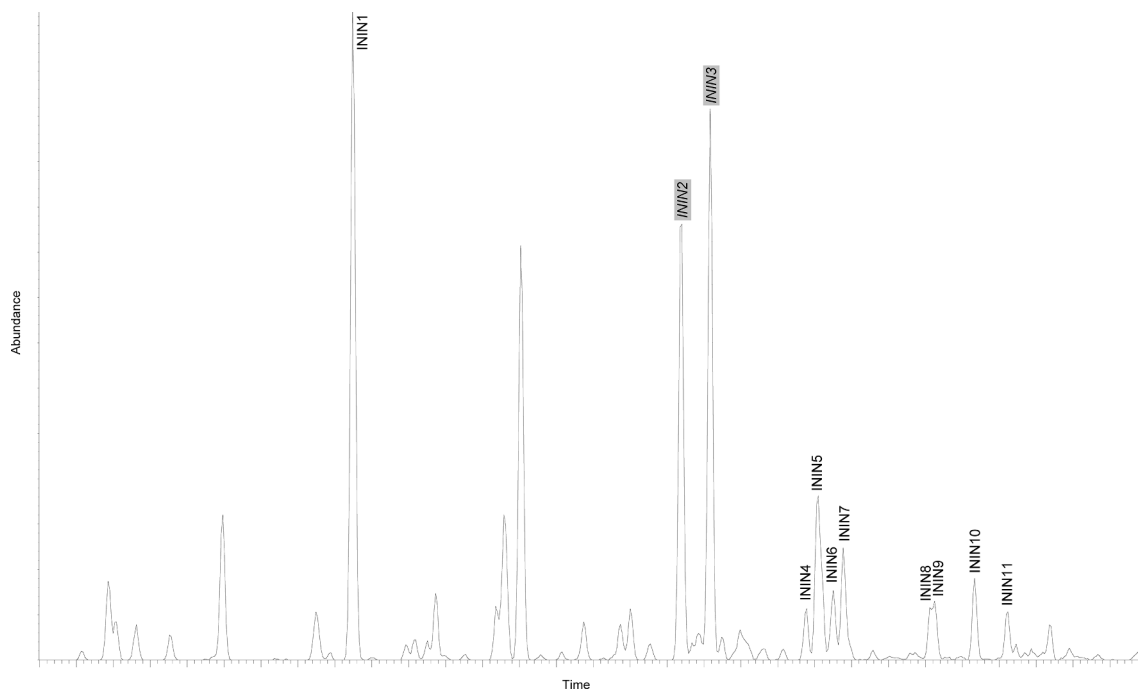
techniques currently used for ignitable liquid analysis because current techniques involve the visual comparison of peak height ratios. Peak height ratios are also a measure independent of the concentration of the sample, which is an advantage over individual peak heights. Compounds generally elute in order of boiling point. Closely eluting compounds

were selected for analysis because evaporation is likely to affect closely eluting compounds similarly. Although no threshold was set for peak proximity, the objective was to evaluate peaks that are close together, as depicted in Figs. 2–6.

Peak pair height ratios were calculated by dividing the peak height of



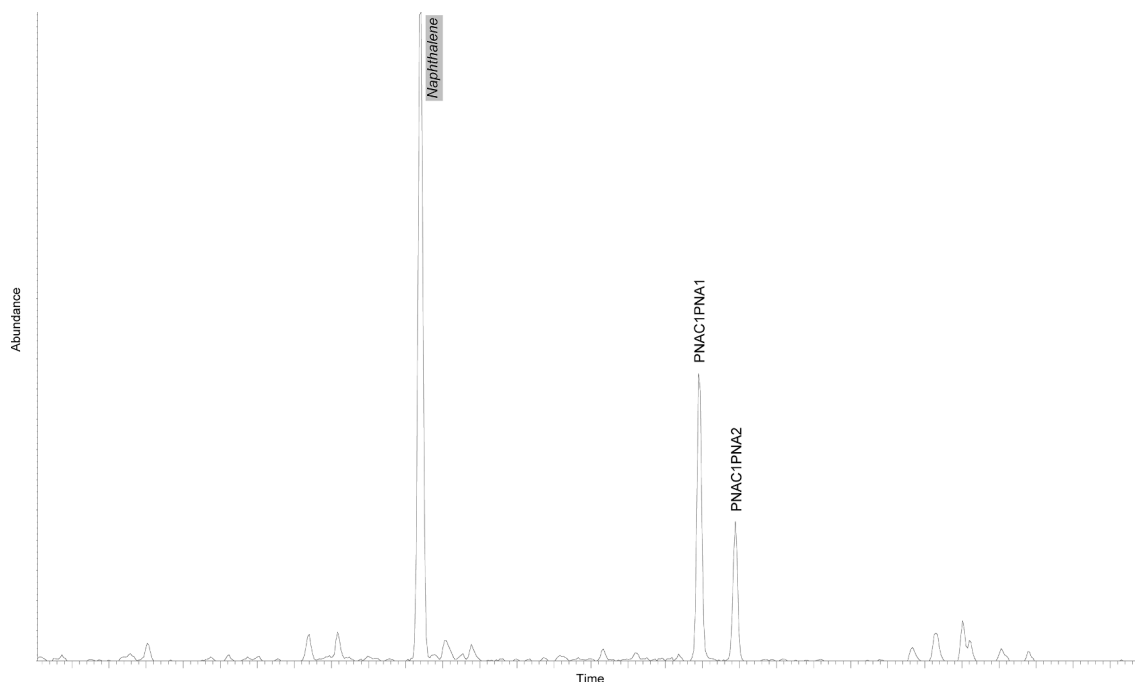
**Fig. 4.** A representative aromatic/alkylbenzene extracted ion profile of a 50% evaporated gasoline sample. Peaks used in assessing peak pair ratios were labeled with their designated peak code, where AR = aromatic/alkylbenzene profile, followed by letters or numbers representing either the known composition of the peak, or in cases where the number of isomers preclude a known composition, letters or numbers to denote the peak. Grayed labels indicate peaks that did not meet study objectives of statistical significance or did not elute near a similar compound to be included in a ratio.



**Fig. 5.** A representative indane extracted ion profile of a 50% evaporated gasoline sample. Peaks used in assessing peak pair ratios were labeled with their designated peak code, where IN = indane profile, followed by letters or numbers representing either the known composition of the peak, or in cases where the number of isomers preclude a known composition, letters or numbers to denote the peak. Grayed labels indicate peaks that did not meet study objectives of statistical significance.

the first eluted compound by the peak height of the second eluted compound in the selected peak pair. The peak heights were obtained from the Agilent Chemstation Area Percent Report and represent the values from the integration line to the peak apex. No one set of integration parameters was able to integrate all peaks of interest in every

sample, particularly peaks that appeared as shoulders of other peaks. The integration parameters also required adjustment based on the general abundance of each sample. Any peak in the TIC that could not be integrated by the software was manually integrated and background subtracted to approximately the same level as the integration line from



**Fig. 6.** A representative polynuclear aromatic extracted ion profile of a 50% evaporated gasoline sample. Peaks used in assessing peak pair ratios were labeled with their designated peak code, where PNA = polynuclear aromatic profile, followed by letters or numbers representing either the known composition of the peak, or in cases where the number of isomers preclude a known composition, letters or numbers to denote the peak. Grayed label indicates a peak that did not meet study objectives because it did not elute near a similar compound to be included in a ratio.

which the peak height of the auto-integrated peaks are based. The abundance of all ions from the tabulation was summed. Any peak in an EIP that could not be integrated by the software was manually integrated and background subtracted like those in the TIC; however, only the abundances of the ions of interest from the tabulation for the profile were manually summed. This approach was used along with checking the approximate peak height of a manually integrated peak with an auto-integrated peak of similar height to limit influence of the integration parameters.

### 2.3. Negative matrix samples

A negative matrix database was developed that consisted of 56 fire debris samples acquired by fire investigators and 56 samples selected from the National Center for Forensic Science (NCFS) substrate database [35]. The creation of realistic, ignitable liquid-free fire debris samples by a laboratory rarely results in the complex compound mixtures typically found in fire debris samples. In order to approximate “real world” samples in this study, local fire investigators were asked to collect samples from structure fires that were determined to be non-incendiary; that represented the moderately to extensively burned debris that is common to forensic laboratory submissions; that were sufficiently distanced from the origin of the fire; and that were not from a location that gasoline may be incidentally present (garage, shed, etc.). These criteria allowed for a reasonable assumption that the samples would be free of gasoline; however other incidental ignitable liquids could not be excluded. These data were complemented with NCFS substrate database data which has a cleaner provenance but limited complexity. The samples used consisted of a variety of flooring materials (carpet, padding, hardwood, laminate), construction and building materials (wood, baseboard, ceiling tile, siding), furniture materials (couch cushions, wooden tabletop, faux leather), and a variety of household materials (plastic wrap, plastic, paper, magazines). Although the spectra were visually distinguishable from the control gasoline spectra, the goal was to evaluate the individual peaks and peak pairs that may be shared between these samples and the control gasoline spectra.

### 2.4. Gasoline statistical analysis

A statistical comparison of the effects of three factors (chromatographic analysis method, acquisition source location, and evaporation level) on each peak pair ratio was conducted using three-way ANOVA. This model considers the three factors and estimates the effect of each factor across the levels (three laboratory locations, three geographic regions, five evaporation levels) of the other factors simultaneously. This statistical method was selected to determine whether any variation observed in a given gasoline peak pair ratio was significant or non-significant with respect to the three variables. For the interpretation of the significant results of all peak ratios, a Bonferroni correction was used, resulting in a p-value threshold of  $0.05/64 = 0.00078$ . A p-value greater than the significance threshold is equivalent to having a confidence interval which contains zero difference for different levels of a factor. Thus, it demonstrated lower variability for that ratio across the factors. It is worth noting that for some peak pair ratios, there is unbalanced data regarding unequal sample sizes for different levels, but ANOVA analysis can still handle this type of unbalanced data for estimating the main effects [36].

### 2.5. Negative matrix statistical analysis

Each negative matrix sample was analyzed for the same chromatographic features of interest as the gasoline samples. The inclusion of the negative matrix sample peak height ratios was done to determine how consistent or variable the presence and pattern of the determined peak pairs were between the gasoline control samples and the negative matrix samples. It should be noted that no minimum abundance or resolution threshold was set for inclusion of a peak. If the peak could be visually distinguished from the baseline, had an apex, and the mass spectrum was consistent with the targeted compound, the peak was included in the analysis.

If both peaks of a selected pair were present in the negative matrix sample, the ratio was calculated. The relative frequency of the presence of the peak pair ratio in the negative matrix samples was compared with

**Table 2**  
Explanation of nomenclature used on peak maps.

Profile(s)	Code	Compound
TIC (T)	TMP	2,3,4-trimethylpentane
TIC (T), Aromatic (AR)	TOL	Toluene
TIC (T), Aromatic (AR)	EB	Ethylbenzene
TIC (T), Aromatic (AR)	XMP	m,p-xylene
TIC (T), Aromatic (AR)	XO	o-xylene
TIC (T), Aromatic (AR)	C3P1	C3 alkylbenzene, peak 1 (propylbenzene)
TIC (T), Aromatic (AR)	C3P2	C3 alkylbenzene, peak 2 (m-ethyltoluene)
TIC (T), Aromatic (AR)	C3P3	C3 alkylbenzene, peak 3 (p-ethyltoluene)
TIC (T), Aromatic (AR)	C3P4	C3 alkylbenzene, peak 4 (1,3,5-trimethylbenzene)
TIC (T), Aromatic (AR)	C3P5	C3 alkylbenzene, peak 5 (o-ethyltoluene)
TIC (T), Aromatic (AR)	124TMB	1,2,4-trimethylbenzene
TIC (T), Alkane (ALK)	C10	Decane
TIC (T), Aromatic (AR)	123TMB	1,2,3-trimethylbenzene
TIC (T), Indane (IN)	IN1	Indane
TIC (T), Aromatic (AR)	C4G1P1	C4 alkylbenzene, group 1, peak 1
TIC (T), Aromatic (AR)	C4G1P2	C4 alkylbenzene, group 1, peak 2
TIC (T), Aromatic (AR)	C4G1P3	C4 alkylbenzene, group 1, peak 3
TIC (T), Aromatic (AR)	C4G1P4	C4 alkylbenzene, group 1, peak 4
TIC (T), Aromatic (AR)	C4G2P1	C4 alkylbenzene, group 2, peak 1
TIC (T), Aromatic (AR)	C4G2P2	C4 alkylbenzene, group 2, peak 2
TIC (T), Aromatic (AR)	C4G3P1	C4 alkylbenzene, group 3, peak 1 (1,2,4,5-tetramethylbenzene)
TIC (T), Aromatic (AR)	C4G3P2	C4 alkylbenzene, group 3, peak 2 (1,2,3,5-tetramethylbenzene)
TIC (T), Indane (IN)	IN2	Substituted indane/indene
TIC (T), Indane (IN)	IN3	Substituted indane/indene
TIC (T)	C5P1	C5 alkylbenzene, peak 1
TIC (T), Aromatic (AR)	C5P2	C5 alkylbenzene, peak 2
TIC (T), PNA (PNA)	Naphthalene	Naphthalene
TIC (T), Indane (IN)	IN4	Substituted indane/indene
TIC (T), Indane (IN)	IN5	Substituted indane/indene
TIC (T), Indane (IN)	IN6	Substituted indane/indene
TIC (T), Indane (IN)	IN7	Substituted indane/indene
TIC (T), Alkane (ALK)	C12	Dodecane
TIC (T), PNA (PNA)	C1PNA1	2-methylnaphthalene
TIC (T), PNA (PNA)	C1PNA2	1-methylnaphthalene
Alkane (ALK)	ALKC9	Nonane
Alkane (ALK)	ALKDIS9	Isoalkane
Alkane (ALK)	ALKISO2	Isoalkane
Alkane (ALK)	ALKDIS11	Isoalkane
Alkane (ALK)	ALK1	Isoalkane
Alkane (ALK)	ALK2	Isoalkane
Alkane (ALK)	ALK3	Isoalkane
Alkane (ALK)	ALK4	Isoalkane

**Table 2 (continued)**

Profile(s)	Code	Compound
Alkane (ALK)	ALK5	Isoalkane
Alkane (ALK)	ALK6	Isoalkane
Alkane (ALK)	ALK7	Isoalkane
Alkane (ALK)	ALK8	Isoalkane
Alkane (ALK)	ALK9	Isoalkane
Alkane (ALK)	C11	Undecane
Alkane (ALK)	ALK10	Isoalkane
Alkane (ALK)	ALK11	Isoalkane
Alkane (ALK)	ALK12	Isoalkane
Aromatic (AR)	C5P3	C5 alkylbenzene, peak 3
Aromatic (AR)	C5P4	C5 alkylbenzene, peak 4
Aromatic (AR)	C5P5	C5 alkylbenzene, peak 5
Aromatic (AR)	C5P6	C5 alkylbenzene, peak 6
Aromatic (AR)	C5P7	C5 alkylbenzene, peak 7
Indane (IN)	IN8	Substituted indane/indene
Indane (IN)	IN9	Substituted indane/indene
Indane (IN)	IN10	Substituted indane/indene
Indane (IN)	IN11	Substituted indane/indene

**Table 3**  
Instrumental parameters.

	Virginia Department of Forensic Science-Norfolk	Pinellas County Forensic Laboratory-Florida	Louisiana State Police Crime Laboratory-Baton Rouge
Instrument	Agilent 7890A GC/5975C MS	Agilent 7890 GC/5975 MS	Agilent 7890B GC/5977B MS
Column	Agilent J&W HP-1MS 30 m × 0.25 mm × 0.25 μm	Agilent J&W DB-1MS 25 m × 0.20 mm × 0.33 μm	Agilent J&W HP-5MS Ultra Inert 30 m × 0.25 mm × 0.25 μm
Injection Volume	1 μL	1 μL	1 μL
Split ratio	50:1	50:1	50:1
Injector	290 °C	250 °C	250 °C
Carrier gas	Helium	Helium	Helium
Flow rate	1.8 mL/min for 2 min 20 mL/min <sup>2</sup> to 1.2 mL/min for 9.97 min 20 mL/min <sup>2</sup> to 1.8 mL/min for 0 min	1 mL/min	1.25 mL/min
Temperature program	40 °C for 1.5 min 20 °C/min to 140 °C for 0 min 30 °C/min to 300 °C for 5.17 min	45 °C for 3 min 20 °C/min to 320 °C for 7.5 min	50 °C for 3 min 10 °C/min to 280 °C for 4 min
Transfer line	300 °C	280 °C	280 °C
Source	230 °C	230 °C	230 °C
Quadrupole	150 °C	150 °C	150 °C
Ionization mode	Election Ionization	Electron Ionization	Electron Ionization
Scan range	14–200 m/z at 0 min 14–400 m/z at 2 min 14–600 m/z at 12 min	33–400 m/z	40–400 m/z

the relative frequency of the peak pair as observed in the gasoline control database. The difference in frequency between the absent ratios in the negative samples versus the absent ratios in the gasoline samples was calculated as a percent point difference (Negative Matrix Peak Ratios Absent % – Gasoline Control Peak Ratios Absent % = Percent Point Difference %).

#### Comparison of gasoline and negative matrix sample ratios

Ratio trends between the gasoline control database and the negative

matrix database were compared for 47 peak pair ratios that had at least three observations in the negative database. A two-sample statistical test was conducted to compare the negative matrix and gasoline control sample peak pair ratios. Due to small sample sizes in the negative database, the nonparametric Wilcoxon rank sum test was performed. The p-values below the Bonferroni corrected significant level ( $0.05/47 = 0.00106$ ) were determined and these small p-values indicate significant difference between negative matrix and gasoline control samples.

## 2.7. Data interpretation

The three-way ANOVA results were organized by a color-coding system to determine which ratios were most consistent and/or indicative of gasoline based on p-values. Color rankings highlight the most consistent peak pair ratios (ANOVA test statistic with a p-value  $> 0.00078$  based on the Bonferroni Correction) across the three variables. The ratios were then organized within each color ranking on the basis of the raw p-value, highest to lowest. For this study, the acquisition source location (SL) was the primary consideration to demonstrate consistency because it demonstrated consistency among marketed gasolines. The remaining variables, chromatographic analysis method (ML) and evaporation level (EL), were considered to be of equal importance. The hierarchical system used to rank the peak pair ratios is described in Table 4 where purple is the highest rank and red is the lowest rank.

The relative frequency results were ranked from high to low percentages. A resulting higher percent value indicated a larger difference in the appearance of the ratio between the two datasets. A lower rank represented a peak pair ratio that was often absent in the negative matrix samples, but present in the control gasoline samples.

The Wilcoxon ranked sum test statistics were ranked from lowest p-value to highest p-value. A large test statistic is associated with a lower p-value, which demonstrates greater variability between the negative database and the gasoline control database. This variability would increase the support of the ratio for the identification of gasoline.

Combining the applied rankings of ANOVA, the frequency analysis, and Wilcoxon ranked sum test, a second color coding system was used to further evaluate the peak pair ratios. The rankings based on the ANOVA results of the peak pair ratios were prioritized. The secondary prioritization was the rankings based on the comparison of peak pair ratio trends between gasoline control and negative matrix samples (Wilcoxon rank). The ANOVA and Wilcoxon ranks were based on the chromatographic peak pair ratios and p-value. Rankings based on the percent difference in frequency between the absence of the ratio in negative matrix samples versus the gasoline control samples (Frequency) was considered, but as a tertiary variable. A summary of the ranking system based on the evaluation of the individual ANOVA, Wilcoxon, and Frequency ranks is detailed in Table 5. This ranking system was used to subdivide the ratios examined by the support they provide for gasoline identification.

**Table 4**  
Hierarchical color ranking for gasoline peak pair ratios.

Color Rank	Description
Purple	Smallest ANOVA test statistics and largest p-values for all three variables (SL, ML, and EL); non-significant
Blue	p-values for SL and one of the other variables (ML or EL) were non-significant
Green	p-values for SL only were non-significant
Yellow	p-values for ML and EL, but not SL were non-significant
Orange	p-values for ML or EL were non-significant
Red	Largest ANOVA test statistics and smallest p-values; SL, ML and EL were all significant

SL = Acquisition Source Location, ML = Chromatographic Analysis Method, EL = Evaporation Level

**Table 5**  
Description of the composite rank assignments.

Color	Rank	Description
Purple	Highest Rank	ANOVA Rank is a low number Wilcoxon Rank is a low number Frequency Rank is a low number
Pink	Middle Rank 1	ANOVA Rank is a low number Wilcoxon Rank is a low number Frequency Rank is a high number
Blue	Middle Rank 2	ANOVA Rank is a low number Wilcoxon Rank is a high number Frequency Rank is a low number
Green	Middle Rank 3	ANOVA Rank is a high number Wilcoxon Rank is a low number Frequency Rank is a low number
Yellow	Middle Rank 4	ANOVA Rank is a low number Wilcoxon Rank is a high number Frequency Rank is a high number
Orange	Middle Rank 5	ANOVA Rank is a high number Wilcoxon Rank is a low number Frequency Rank is a high number
Gray	Middle Rank 6	ANOVA Rank is a high number Wilcoxon Rank is a high number Frequency Rank is a low number
Red	Lowest Rank	ANOVA Rank is a high number Wilcoxon Rank is a high number Frequency Rank is a high number

## 2.8. Generating the peak ratio point value assignments

A system was developed to assign relative point values for each of the peak pair ratios. Based upon the ranking assignments in Table 5, a maximum point value for each of the peak pair ratio color-coded ranks was assigned in a descending order (Table 6). Differences in the peak pair ratio values in an unknown sample may be due to a number of factors, such as matrix contribution to or degradation of one compound of the peak pair. Lower points are assigned to ratio values farther from the mean of the corresponding ratio in the gasoline samples studied. Allowing for variation in the ratio approximates the contemporary pattern comparison techniques. To generate the point value, a peak pair ratio in the unknown sample within one standard deviation of the mean of the same observed ratio in the gasoline control samples received more points, while those farther from the mean received fewer or no points. Based on the statistical analysis, the peak ratios that make up the gray and red color ranks were excluded as they did not meet the statistical goals of this study.

The point values per color code earned by each peak pair ratio of a sample were based on which of the standard deviation ranges ( $\pm 1$ ,  $\pm 2$ , or  $\pm 3$  calculated from the control gasoline database) the ratio value falls within (Fig. 7). If the peak pair ratio for a sample was either absent or did not fall within the prescribed standard deviation ranges, no points were assigned.

Log transformed standard deviation ranges were generated for each of the peak pair ratios in the gasoline control database. A log transformed standard deviation range was selected to represent the acceptable range of values for the point assignments of a given peak pair ratio because it represents the distribution of individual samples in the given

**Table 6**  
Point values by rank.

Color Rank	Maximum Point Value	Other Possible Point Values
Purple	6	5, 4
Pink	5	4, 3
Blue	4	3, 2
Green	3	2, 1
Yellow	2	1, 0
Orange	1	0
Gray	Excluded	Excluded
Red	Excluded	Excluded



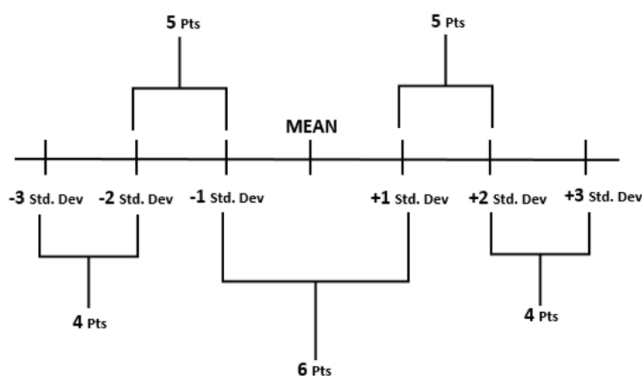


Fig. 7. Point (Pts) assignments based on standard deviation (Std. Dev) and distribution for a peak pair ratio earning a maximum of 6 points (purple). This example depicts the points attainable for the peak pair ratio from an unknown sample based on a comparison of the log transformed ratio to the log transformed values calculated from the gasoline control database.

data set. The log transformation reduces the skew of the data. Within the data set of gasoline control samples, for a specific ratio, observations within one standard deviation of the mean account for approximately 68% of the population. Observations within two standard deviations account for approximately 95%, and those within three standard deviations account for approximately 99.7%.

The determined standard deviation ranges at the  $\pm 1$ ,  $\pm 2$ , and  $\pm 3$  deviations for each peak pair ratio, based on the log transformed values and the mean of the control gasoline samples, are displayed in Table 7. The table is used by comparing the log transformed peak pair ratio value determined for a sample to the value for each of the standard deviation ranges. The point assignment for the peak pair ratio is determined by the potential points for that ratio and the standard deviation range within which the sample value falls. This process was completed for the gasoline control samples and negative matrix samples in this study.

## 2.9. Graphical presentation of support for gasoline

The totality of the support for an identification of gasoline in an unknown sample can be viewed graphically by plotting the total points received by peak pair ratios in the TIC versus the total points received by peak pair ratios in all of the EIPs. The possible total point values for these axes are displayed in Table 8.

## 2.10. Generating the sufficiency graph with data supported decision line placements

A continuum of data representing gasoline in samples is necessary to determine the placement of the decision lines on the sufficiency graph. The gasoline and negative samples previously described are each necessary as known non-complex gasoline samples and known samples with no gasoline contribution. For the continuum, a database consisting of two additional sample sets was created by performing passive adsorption-elution (ASTM E1412-19) [37] extractions on negative debris samples and eluting the activated charcoal strip with carbon disulfide containing serially diluted 75% evaporated gasoline. The gasoline:carbon disulfide ratios for an initial set included 1:100, 1:500, 1:1000, and 1:2000. Four samples of each dilution were examined using the Pinellas County Forensic Laboratory, Florida GC-MS. Based on the results of these initial samples, an additional 50 samples were created which consisted of 10 samples of each of the following gasoline: carbon disulfide ratios: 1:1000, 1:2000, 1:400, 1:8000, and 1:16000. These samples were examined using the Virginia Department of Forensic Science GC-MS method. A total of 66 samples containing gasoline and matrix were generated, representing a range of complexity of gasoline with matrix contribution. Three analysts processed each of these

samples in the same manner as the gasoline control database and negative matrix database and the results for each sample were averaged together. This approach was used as a non-robust, outlier sensitive, calculation to determine the central tendency for the data set. It should be noted that no minimum abundance or resolution threshold was set for inclusion of a peak. If the peak could be visually distinguished from the baseline, had an apex, and the mass spectrum was consistent with the targeted compound, the peak was included in the analysis.

The results were plotted onto X-Y scatter plots to test the efficacy of the established point system and document the continuum of data. Decision lines were created and placed on the plotted graph to delineate the three possible regions which capture and define the non-complex gasoline control samples, complex gasoline with matrix contribution samples, and negative debris samples.

To mathematically determine the decision lines, ROUT Outlier Analysis (Robust regression followed by OUTlier identification) was used to first define unique, non-overlapping datasets. The ROUT method is a non-linear regression based false discovery rate method that identifies outliers that have little impact on the data, but are far enough from the prediction of the given model to be called outliers. It is able to determine multiple outliers and therefore is appropriate for non-linear clustering analysis. This analysis resulted in the removal of gasoline with matrix contribution data points if they clustered with the bulk density of negative matrix or gasoline control data points.

Using the unique, non-overlapping datasets determined by ROUT, Linear Discriminant Analysis (LDA) was performed to generate the two dividing decision lines that make up the three reference regions on the fire debris sufficiency graph. Discriminant Analysis is a multivariate classification technique that can be used to separate points into two or more mutually exclusive groups based on predictors. The data classes are known beforehand to create a model that can be used to predict future observations. The results are visualized via partition plots.

## 2.11. Processing tool protocol

An Excel processing tool was developed to automate the sample analysis and determination of the plot values for a given sample. Use of this developed tool requires the examiner to import the results of a Chemstation Area Percent Report and select the appropriate retention times for the peaks of interest. The examiner must verify the spectral information for the peaks of interest while analyzing the data. Following the data input, the tool automatically calculates the peak height ratios, sums the accumulated points for the x and y axes, and plots the resultant values on the sufficiency graph. The use of this processing tool was able to minimize the time required to process each sample. Following training and practice, each sample was processed within approximately 10 min.

## 2.12. Validation

Following the mathematical placement of decision lines on the gasoline sufficiency graph several steps were taken to examine the efficacy of the sufficiency graph and the placement of the decision lines. These steps included examining representative samples from other ignitable liquid classifications and mixtures of ignitable liquids, examining gasoline analyzed on GC-MS methods that were not included in the development of the gasoline sufficiency graph, and examination of previously determined data files using this method. Additionally, a reproducibility study was conducted to evaluate potential differences in data analysis by multiple analysts and develop strategies to mitigate any differences.

### 2.12.1. Other ignitable liquid classifications

Each ASTM E1618 classification of ignitable liquid is composed of defined compound types, which are subdivided by boiling range into light, medium, and heavy (with the exception of gasoline). Although the

**Table 7**  
Standard deviation ranges and associated point assignments per peak pair ratio.

Color Rank	Peak Pair Ratio	1 Standard Deviation			2 Standard Deviations			3 Standard Deviations		
		Lower Bound	Upper Bound	Max Points	Lower Bound	Upper Bound	Middle Points	Lower Bound	Upper Bound	Lowest Points
Purple	TTMP:TTOL	-1.78	-0.88	6	-2.23	-0.43	5	-2.68	0.02	4
Pink	TEB:TXMP	-1.32	-0.78	5	-1.59	-0.51	4	-1.86	-0.24	3
Pink	TXMP:TXO	0.32	0.83	5	0.07	1.08	4	-0.19	1.34	3
Pink	TC3P1:TC3P2	-1.45	-1.00	5	-1.68	-0.77	4	-1.91	-0.54	3
Orange	TC3P2:TC3P3	0.40	1.17	1	0.01	1.56	0	-0.38	1.95	0
Orange	TC3P3:TC3P4	-0.37	0.23	1	-0.67	0.53	0	-0.98	0.83	0
Pink	TC3P4:TC3P5	0.15	0.34	5	0.05	0.43	4	-0.04	0.53	3
Orange	TC3P5:T124TMB	-1.51	-1.22	1	-1.66	-1.08	0	-1.80	-0.93	0
Orange	TC3P2:T124TMB	-0.64	-0.18	1	-0.87	0.04	0	-1.09	0.27	0
Orange	T124TMB:T123TMB	1.04	1.41	1	0.85	1.60	0	0.66	1.79	0
Purple	TC10:T123TMB	-1.73	-0.86	6	-2.16	-0.42	5	-2.60	0.01	4
Green	TC4G1P1:TC4G1P2	-1.14	-0.80	3	-1.31	-0.62	2	-1.48	-0.45	1
Purple	TC4G1P2:TC4G1P3	0.42	0.79	6	0.24	0.97	5	0.06	1.15	4
Purple	TC4G1P3:TC4G1P4	-0.73	-0.30	6	-0.94	-0.08	5	-1.15	0.13	4
Blue	TC4G2P1:TC4G2P2	-0.64	-0.35	4	-0.78	-0.21	3	-0.93	-0.07	2
Pink	TIN2:TIN3	-0.23	0.00	5	-0.34	0.12	4	-0.46	0.23	3
Orange	TC5P1:TC5P2	-0.18	0.18	1	-0.36	0.36	0	-0.55	0.54	0
Orange	TIN4:TIN5	-0.91	-0.47	1	-1.13	-0.24	0	-1.36	-0.02	0
Green	TIN5:TIN6	0.79	1.05	3	0.66	1.18	2	0.52	1.32	1
Green	TIN6:TIN7	-1.30	-0.85	3	-1.52	-0.63	2	-1.74	-0.41	1
Orange	TC1PNA1:TC1PNA2	0.45	1.11	1	0.11	1.45	0	-0.22	1.78	0
Blue	ALK2:ALK3	-1.21	-0.34	4	-1.65	0.10	3	-2.09	0.54	2
Blue	ALK3:ALK4	0.41	2.44	4	-0.60	3.45	3	-1.62	4.47	2
Purple	ALK4:ALK5	-1.47	-0.75	6	-1.83	-0.40	5	-2.18	-0.04	4
Blue	ALK5:ALK7	-0.42	0.27	4	-0.77	0.62	3	-1.12	0.97	2
Pink	ALK6:ALK8	-0.46	-0.01	5	-0.69	0.22	4	-0.91	0.44	3
Blue	ALK7:ALK9	0.10	0.92	4	-0.31	1.33	3	-0.72	1.74	2
Pink	ALKC11:ALKC12	0.24	0.85	5	-0.07	1.16	4	-0.37	1.46	3
Pink	ALK10:ALK11	0.45	1.34	5	0.01	1.78	4	-0.44	2.22	3
Orange	AREB:ARXMP	-1.13	-0.76	1	-1.31	-0.58	0	-1.49	-0.39	0
Orange	ARXMP:ARXO	0.40	0.73	1	0.23	0.89	0	0.07	1.06	0
Pink	ARC3P1:ARC3P2	-1.31	-0.96	5	-1.49	-0.78	4	-1.67	-0.60	3
Pink	ARC3P2:ARC3P3	0.56	0.82	5	0.42	0.96	4	0.29	1.09	3
Pink	ARC3P4:ARC3P5	0.10	0.29	5	0.00	0.38	4	-0.09	0.47	3
Orange	ARC3P5:AR124TMB	-1.51	-1.12	1	-1.70	-0.93	0	-1.90	-0.73	0
Orange	ARC3P2:AR124TMB	-0.45	-0.25	1	-0.55	-0.16	0	-0.64	-0.06	0
Orange	AR124TMB: AR123TMB	0.98	1.44	1	0.74	1.68	0	0.51	1.91	0
Orange	ARC4G1P1:ARC4G1P2	-0.87	-0.71	1	-0.95	-0.64	0	-1.03	-0.56	0
Purple	ARC4G1P2:ARC4G1P3	0.32	0.63	6	0.16	0.79	5	0.00	0.95	4
Green	ARC4G1P3:ARC4G1P4	-0.70	-0.40	3	-0.85	-0.25	2	-0.99	-0.11	1
Pink	ARC4G2P1:ARC4G2P2	-0.58	-0.46	5	-0.64	-0.40	4	-0.70	-0.35	3
Pink	ARC4G3P1:ARC4G3P2	-0.44	-0.27	5	-0.53	-0.18	4	-0.62	-0.09	3
Green	ARC5P3:ARC5P4	-0.07	0.17	3	-0.18	0.28	2	-0.30	0.40	1
Purple	ARC5P7:ARC5P2	-0.40	0.16	6	-0.67	0.44	5	-0.95	0.71	4
Green	ININ4:ININ5	-1.23	-1.06	3	-1.31	-0.97	2	-1.40	-0.89	1
Pink	ININ5:ININ6	0.90	1.02	5	0.84	1.08	4	0.78	1.14	3
Orange	ININ6:ININ7	-0.72	-0.53	1	-0.82	-0.43	0	-0.92	-0.33	0
Purple	ININ8:ININ9	-0.18	0.03	6	-0.29	0.14	5	-0.40	0.25	4
Purple	ININ9:ININ10	-0.59	-0.40	6	-0.68	-0.30	5	-0.78	-0.21	4
Green	ININ10:ININ11	0.36	0.80	3	0.14	1.02	2	-0.07	1.24	1
Orange	PNAC1PNA1: PNAC1PNA2	0.45	1.03	1	0.16	1.32	0	-0.13	1.61	0
Yellow	AR123TMB:ININ1	0.15	0.69	2	-0.12	0.96	1	-0.40	1.23	0

**Table 8**  
Maximum point potentials for TIC and EIPs.

Color Rank	Number of TIC Peak Pair Ratios	Maximum Points	Total Points per Color Code (TIC)	Number of EIP Peak Pair Ratios	Maximum Points	Total Points per Color Code (EIP)
Purple	4	6	24	5	6	30
Pink	6	5	30	9	5	45
Blue	1	4	4	4	4	16
Green	3	3	9	4	3	12
Yellow	0	2	0	1	2	2
Orange	7	1	7	8	1	8
<b>Total Points</b>			<b>74</b>			<b>113</b>

patterns collectively differ between each of the ignitable liquid classes, individual key diagnostic peaks identified in gasoline may be present in liquids belonging to other classifications. Therefore, it was important to evaluate that the gasoline sufficiency graph's point system and the placement of the decision lines to minimize false positives related to the different classes of ignitable liquids.

A subset database of other ignitable liquids was created with samples from five classes of ignitable liquids. Generally, three examples each of a light, medium and heavy product for the aromatic, isoparaffinic, naphthenic-paraffinic, and petroleum distillate classifications were processed and evaluated. Normal alkanes and oxygenated products were excluded as they are composed of very few compounds and do not generally share chromatographic features with gasoline. Additionally, eight mixtures of ignitable liquids were evaluated. Two of these mixtures were composed of gasoline and a heavy petroleum distillate while the others did not contain gasoline. A total of  $n = 43$  samples were processed for this portion of the study.

#### 2.12.2. Methods

Additional samples of 50% and 90% evaporated gasoline were analyzed using GC-MS fire debris methods currently in use at 10 additional forensic laboratories in order to expand the tested methods beyond the methods used to build the model. The resulting data files were processed, assigned point values, and plotted onto the gasoline sufficiency model to test the efficacy of the decision line placement and overall utility of the sufficiency graph.

#### 2.12.3. Previously determined data files – realistic sample processing

Realistic casework-like samples were also utilized to test the efficacy of the sufficiency graph template. For this validation step, a member of the research team collected, from stored data, a pool of 60 existing identified data files and their associated determinations. A second member of the research staff subsequently unlinked (stripped of identifiers) and assigned new anonymized identifiers to each of the 60 datasets; a key linking the data to their original designations was not maintained.

Once the new identifiers were assigned, 30 data files were selected at random and divided between two analysts for processing. The selected samples consisted of an even distribution of the following previously determined conclusions: no ignitable liquid identified; gasoline identified; or a non-gasoline ignitable liquid identified. During evaluation with the sufficiency method, the examiners also commented on the complexity of each sample based on their subjective experience.

#### 2.12.4. Reproducibility study

To test that the final TIC and EIP point determinations were reproducible, several iterations of sample processing were performed by Virginia Department of Forensic Science staff. During the first round of processing, the six staff members were each given data files for the same three samples, which included one negative sample and two matrix samples spiked with gasoline, and data files for reference gasoline. The staff members were provided Figs. 2–6 and a basic overview of the steps to process a data file. Sources of variability within the method were identified and training was conducted to mitigate these sources. An additional three samples (one negative sample and two matrix samples spiked with gasoline) were subsequently processed by each of the examiners.

### 3. Results and discussion

#### 3.1. Statistical analysis of gasoline

This study objectively viewed peak pairs found in the chromatographic analysis of gasoline and used that data to develop a statistically supported method to evaluate an unknown sample for the presence of gasoline. The first step in this process was to evaluate gasoline samples

to determine peak pairs that showed the greatest ratio stability, accounting for chromatographic analysis method, acquisition source location, and evaporation level (Table 9). In each evaluation, the potential variability of the other factors was controlled for by how the data was aggregated and compared. For the chromatographic analysis method, an aggregate of all source locations within each evaporation level was compared to the equivalent data pool for each chromatographic analysis method. For the acquisition source location, the data was first aggregated by chromatographic analysis method, then by acquisition source location, and then by evaporation level within each source. The comparison was then performed between acquisition source locations at each evaporation level and within, but not across, chromatographic analysis method. Lastly, for evaporation level, aggregates of all source locations and method locations at each evaporation level were compared to the other aggregates of pooled data for the other respective evaporation levels. The top six ranked peak pair ratios, each categorized as purple, were stable with respect to each of the variables.

Based on the statistically supported significance trends in Table 9, evaporation level was not determined to be a significant source of variability in peak height ratios. Although there are visual pattern differences notable in the TIC and EIPs of gasoline at difference evaporation levels, at a cumulative data level, these differences do not significantly affect the individual peak pairs selected for analysis (Fig. 8). Table 9 demonstrates that for the peak pairs evaluated, evaporation level was the factor that held consistent more often than acquisition source location and chromatographic analysis method. This was the reason for choosing closely eluting peaks to form the peak pair ratios. Approximately the same number of peak pair ratios evaluated were consistent with respect to acquisition source location and chromatographic analysis method. Although chromatographic analysis method could be eliminated as a source of variation if a standard instrument method was used throughout the field of ignitable liquid analysis, the goal of this project was to create an interpretation method that can be used by multiple forensic laboratories using their existing methods. Laboratory method optimization is often dependent on the time, resources, and procedure flexibility available at a location and these are variable between laboratories.

The next step was to evaluate the peak pair ratios from gasolines with respect to the appearance and stability of the same ratios in the negative matrix samples. This evaluation decreased the composite rank of peak pairs that are commonly detected in negative matrix samples and increased the rank of peak pairs that were more unique to gasoline. Fig. 9 graphically displays a comparison of the percent presence of each peak pair ratio in the control gasoline and the negative matrix samples. For frequency rankings, peak pair ratios that were less frequently observed in the negative matrix samples, relative to the gasoline control samples, were assigned a higher rank. The Wilcoxon rank sum statistics further compared the ratios when the peak pair ratio was present in both the gasoline control and negative matrix samples. The rank based on Wilcoxon rank sum statistics is a nonparametric comparison of the difference between the gasoline control sample ratios and the negative matrix sample ratios with a Bonferroni corrected p-value. A higher value of Wilcoxon rank sum statistic has a lower p-value and is representative of the variability between the gasoline and negative matrix ratio, which is preferred, and ranked higher. The ratios that were not present in the negative matrix database are given a rank of zero.

#### 3.2. Composite peak pair rankings

The composite ranking system sorted each peak pair into one of eight categories. For clarity, colors were assigned to each category (Table 10). For each ranking system (ANOVA, Wilcoxon, and Frequency) each peak pair ratio was categorized as either 'high' or 'low'. The ranks of 0–30 were considered "high" and the remaining ranks were considered "low". The eight color-based categories were determined by which of the results (ANOVA, Wilcoxon, Frequency) received a high or low rank

**Table 9**

Gasoline peak pair ratio rankings using ANOVA statistics; marked cells indicate the peak pair ratio was consistent.

Rank	Color Rank	Peak Pair Ratio	Chromatographic Analysis Method	Acquisition Source Location	Evaporation Level
1	Purple	TC3P1:TC3P2	●	●	●
2	Purple	ARC4G3P1:ARC4G3P2	●	●	●
3	Purple	ARC3P1:ARC3P2	●	●	●
4	Purple	ARC4G2P1:ARC4G2P2	●	●	●
5	Purple	TC4G2P1:TC4G2P2	●	●	●
6	Purple	ALK3:ALK4	●	●	●
7	Blue	ALK5:ALK7		●	●
8	Blue	ALK2:ALK3		●	●
9	Blue	ININ9:ININ10		●	●
10	Blue	TIN2:TIN3		●	●
11	Blue	TC4G1P3:TC4G1P4		●	●
12	Blue	ININ8:ININ9		●	●
13	Blue	TXMP:TXO	●	●	●
14	Blue	TC4G1P2:TC4G1P3		●	●
15	Blue	ALK7:ALK9		●	●
16	Blue	ARC3P4:ARC3P5		●	●
17	Blue	ALK6:ALK8		●	●
18	Blue	TC3P4:TC3P5		●	●
19	Green	ARC3P2:ARC3P3		●	●
20	Green	ARC4G1P2:ARC4G1P3		●	●
21	Yellow	TEB:TXMP	●		●
22	Yellow	ALKC11:ALKC12	●		●
23	Yellow	AR123TMB:ININ1	●		●
24	Yellow	TTMP:TTOL	●		●
25	Yellow	ALK10:ALK11	●		●
26	Yellow	ININ5:ININ6	●		●
27	Orange	ALK4:ALK5			●
28	Orange	TIN4:TIN5			●
29	Orange	ARC5P7:ARC5P2			●
30	Orange	TIN6:TIN7			●
31	Orange	ININ2:ININ3			●
32	Orange	ARC4G1P3:ARC4G1P4			●
33	Orange	ARC5P5:ARC5P6			●
34	Orange	ARC5P6:ARC5P7			●
35	Orange	TC3P2:TC3P3			●
36	Orange	TC3P3:TC3P4			●
37	Orange	TIN5:TIN6			●
38	Orange	PNAC1PNA1:PNAC1PNA2			●
39	Orange	ININ10:ININ11			●
40	Orange	ININ6:ININ7			●
41	Orange	TC4G3P1:TC4G3P2			●
42	Orange	TC4G1P1:TC4G1P2			●
43	Orange	TC1PNA1:TC1PNA2			●
44	Orange	ARC3P5:ALKISO2			●
45	Orange	ALK1:ALK2			●
46	Orange	TC5P1:TC5P2			●
47	Orange	ALK9:ALKC11			●
48	Orange	ININ4:ININ5			●
49	Orange	ARC4G1P1:ARC4G1P2			●
50	Orange	ARC5P4:ARC5P5			●
51	Orange	TC3P5:T124TMB	●		●
52	Orange	ARC5P3:ARC5P4			●
53	Orange	TC10:T123TMB			●
54	Orange	ARC3P2:AR124TMB	●		●
55	Orange	T123TMB:TIN1			●
56	Red	ARC3P3:ARC3P4			
57	Red	AR124TMB:AR123TMB			
58	Red	ALKC9:ALKDIS9			
59	Red	T124TMB:T123TMB			
60	Red	ARC3P5:AR124TMB			
61	Red	ARXMP:ARXO			
62	Red	AREB:ARXMP			
63	Red	TC3P2:T124TMB			
*		ALKC10:ALKDIS11			

\* = ALKDIS11 was only resolved using Virginia's acquisition method

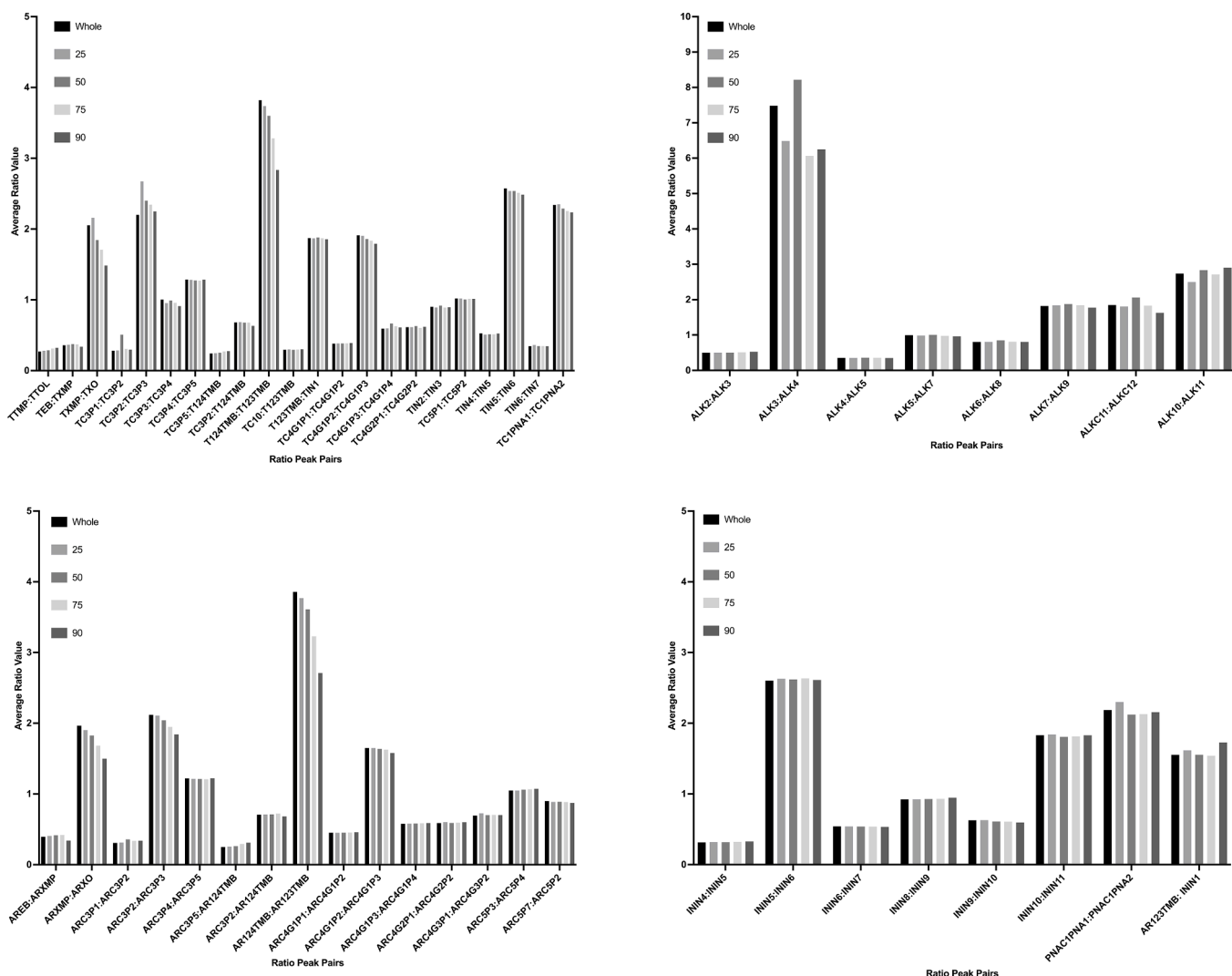
● = non-significant p-value (&gt;0.00078), therefore consistent

(Table 5). The two lowest ranking categories (gray and red) were eliminated from further study as they provided very little or no statistical support for gasoline.

Based upon this categorical system, a method for applying point values to each of the peak pair ratios was developed using the mean and standard deviations of the observed ratios in the control gasoline

samples. The log transformed standard deviation limits for the ratios examined are detailed in Table 7. These ranges were used to calculate the total TIC and EIP points attained by each of the gasoline control samples and each of the negative matrix samples. This table is also applicable to unknown samples.

The sum of the points for the TIC and EIP axes are based on the



**Fig. 8.** Graphical representation of the mean values of peak height ratios per peak pair displayed for gasoline Evaporation Levels; not shown are Method or Source Location. See Table 9 for a robust statistical analysis of the effects of each variable on the given peak pairs.

developed point system and allow each peak pair ratio to cumulatively add weight to the interpretation. Fig. 10 is the graphical representation of the total points obtained for the gasoline control and negative matrix samples. The data demonstrated that the gasoline and negative matrix samples used in this study can be clearly separated from each other by this quantitative method, and this method is more objective than visually differentiating chromatograms.

### 3.3. Creation of gasoline sufficiency graph with decision lines

Fig. 11 displays the addition of the data points from the matrix samples containing gasoline to the gasoline control and negative matrix samples. This scatter plot shows the separation of the gasoline and negative samples as well as the continuum of data developed from matrix with gasoline. This continuum includes data points that overlap with the control gasoline, data points that overlap with the negative matrix samples, and data points that fall within the region between the control gasoline and negative matrix samples.

A partition plot was created using non-overlapping LDA datasets. The LDA datasets include the TIC and EIP points for the peak pair ratios, which can be classified into one of three discrete dependent classifications: negative, complex, and non-complex. Complex data points were excluded if the ROUT outlier analysis results demonstrated that they clustered with the bulk density of negative matrix or gasoline control

data points. This approach removed the samples that would have a visual gasoline pattern easily distinguishable from the matrix contribution and removed samples that clustered with the negative matrix samples, indicating that they had very little data in common with gasoline. Additionally, two negative matrix data points were excluded that contained ignitable liquid. The data points included and excluded from the LDA datasets are depicted on Fig. 12.

LDA was selected to generate the decision lines because the basis of LDA is distinct known classification and because it has applications as a predictive tool with low predictive error rate. The approximate expected error rate from the LDA generated decision lines was determined to be 0.026, meaning that the model predicts that approximately 2.6% of future samples would be classified in an incorrect region of the sufficiency graph.

The partition plots were generated using R and visually overlaid with a graph of the original data points that was generated using Prism to determine the linear equations of the partition lines (Fig. 13).

The equations for the lines were determined to be  $y = -1.190x + 97.18$  for the upper line and  $y = -1.298x + 49.14$  for the lower line. These equations were then used to create the sufficiency graph in Fig. 14, which includes the negative, gasoline, and matrix with gasoline data points, the data-based decision lines, and a heat map to represent the regions of the graph: red (negative), yellow-orange (complex), and green (non-complex).

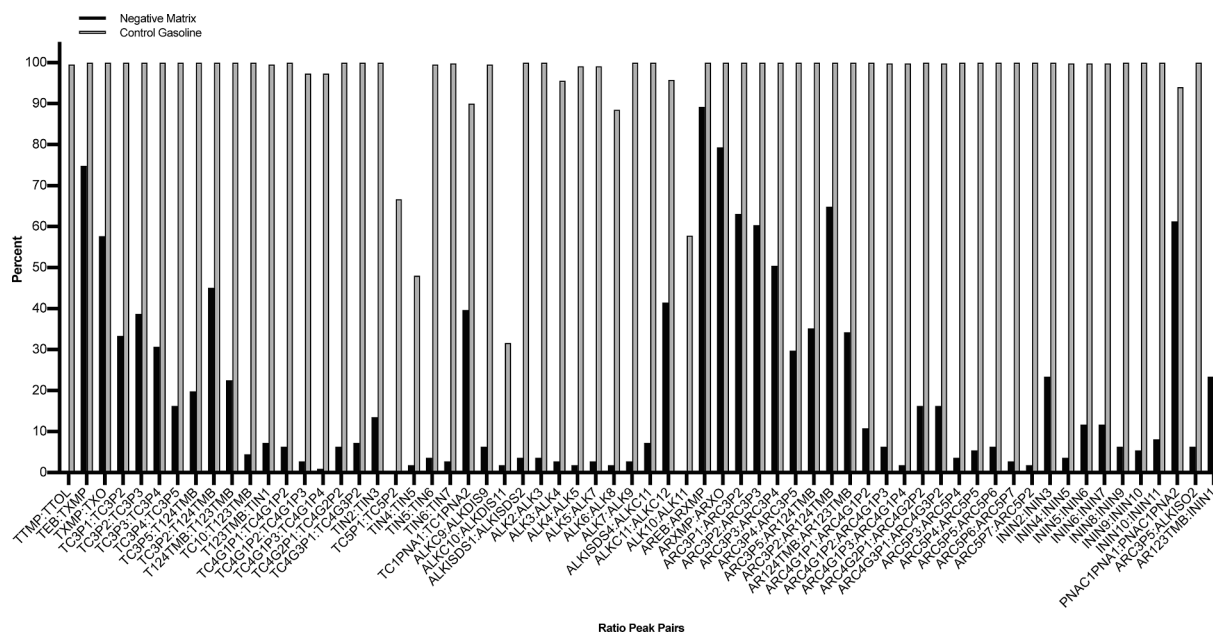


Fig. 9. Frequency of the presence of a peak pair in negative matrix and gasoline control samples, displayed as a percent.

The data points were removed for the evaluation and validation of the line placement. The application of the graph and decision lines are judged and applied in a similar manner as the friction ridge sufficiency graph. For gasoline, any data points falling in the red region, below the lower line, do not have sufficient information for evaluation for gasoline and, therefore, gasoline should not be identified. The area shaded green, above the dotted, upper line demonstrates an area where the data points have sufficient value for the identification of gasoline. The TIC and EIP data for these data points generally would show a high level of visual agreement with a gasoline reference. These data points are considered non-complex and require general documentation for the identification. The area between the two decision lines, shaded as yellow, is considered complex. Data points that fall in this region may or may not have enough data to support the identification of gasoline. The closer a data point in this complex region is to a decision line, the more likely the result is to align with the result on the opposite side of the line. The data points in this region require detailed documentation to support the final conclusion.

### 3.4. Validation

#### 3.4.1. Additional ignitable liquid classifications

The sufficiency plot values for the 43 non-gasoline ignitable liquids and ignitable liquid mixtures studies are shown in Fig. 15. The naphthenic-paraffinic and isoparaffinic products did not score significant point values and are congregated on one of the axes. These classifications would therefore not score enough points to be errantly classified as gasoline on the gasoline sufficiency graph. Some aromatic and petroleum distillate products plotted in the complex area. Aromatic solvents share many of the same key diagnostic aromatic peaks found in gasoline, including the prominent C3 and C4 alkylbenzene peak groupings. Additionally, petroleum distillate products are added to gasoline to improve octane ratings. However, gasoline is distinguished from the aromatic and distillate classifications because both the aromatic and alkane chromatographic features of interest must be present and the aromatic chromatographic features of interest must appear at a higher relative abundance than the alkane features for gasoline to be identified. Due to the similarities, the aromatic solvents and petroleum distillate products were predicted to score high, but not equal to gasoline. The ignitable liquid mixtures which contain gasoline or aromatic

solvents mixed with petroleum distillates plotted in both the complex and non-complex regions. Taken together, these results show the efficacy of the line placement and validate the accuracy of the point system when considering non-gasoline ignitable liquids.

#### 3.4.2. GC-MS acquisition methods validation

The chromatographic features of interest used in this process were selected based on their resolution in three different instrumental methods that included both HP-1 and HP-5 gas chromatography columns. The majority of the selected peaks are well documented gasoline chromatographic features that are targeted in GC-MS methods that have been optimized for ignitable liquid analysis. However, some selected chromatographic peaks may not resolve similarly across different instrumental methods.

An initial evaluation of gasoline data obtained from 10 additional GC-MS methods from a selection of operating forensic laboratories showed that, in general, methods that use HP-1 columns scored higher than HP-5 columns and gasoline from the majority of those methods plotted in the non-complex region, as expected (Fig. 16).

Based on these results, all chromatographic methods should be evaluated with a known gasoline sample to determine if the data allows for use of this point system. When evaluating the usability of the sufficiency point system with an individual method, it is important to check that most of the data points are obtainable and that the relative pattern for the peak pair ratios is similar to those used when the model was built. This preliminary evaluation can be done by processing and plotting the known gasoline sample on the existing sufficiency graph. Based on the outcome of the points, if the known gasoline data plots as expected in the non-complex region, use of the existing model is recommended. If the data plots outside of the non-complex region, optimization of the instrumental method or, alternatively, of the point system is necessary to proceed.

#### 3.4.3. – Previously determined data files – realistic sample processing

Each sample was processed and plotted using the developed method. After the samples were processed and plotted, the original determinations for each data point were also labeled on the graph (Fig. 17).

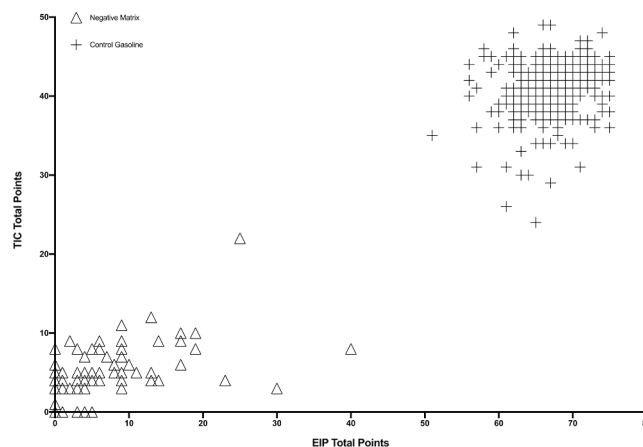
Each of the samples (10/10) that were previously determined to contain gasoline plotted in the non-complex region. The majority (15/

**Table 10**  
Color-coded final rankings for all peak pair ratios.

Color Rank	Ratio Name	ANOVA	Wilcoxon	Frequency	
Purple	TTMP:TTOL	24	0	1	
	TC4G1P2:TC4G1P3	14	23	16	
	TC4G1P3:TC4G1P4	11	0	8	
	TIN6:TIN7	30	26	7	
	ALK4:ALK5	27	0	4	
	ARC4G1P2:ARC4G1P3	20	21	24	
	ARC5P7:ARC5P2	29	0	2	
	ININ8:ININ9	12	14	22	
	ININ9:ININ10	9	24	18	
	Pink	TEB:TXMP	21	0	62
TXMP:TXO		13	0	56	
TC3P1:TC3P2		1	0	46	
TC3P4:TC3P5		18	0	36	
TIN2:TIN3		10	27	35	
TIN4:TIN5		28	0	55	
ALK6:ALK8		17	0	34	
ALKC11:ALKC12		22	7	52	
ALK10:ALK11		25	0	50	
ARC3P1:ARC3P2		3	3	58	
ARC3P2:ARC3P3		19	10	57	
ARC3P4:ARC3P5		16	19	43	
ARC4G2P1:ARC4G2P2		4	9	37	
ARC4G3P1:ARC4G3P2		2	12	38	
ININ5:ININ6		26	15	32	
Blue	TC4G2P1:TC4G2P2	5	37	20	
	ALK2:ALK3	8	40	11	
	ALK3:ALK4	6	43	26	
	ALK5:ALK7	7	44	9	
Green	ALK7:ALK9	15	32	5	
	TC10:T123TMB	53	25	15	
	TC4G1P1:TC4G1P2	42	29	19	
	TIN5:TIN6	37	20	14	
	ARC4G1P3:ARC4G1P4	32	0	3	
Yellow	ARC5P3:ARC5P4	52	17	12	
	ININ4:ININ5	48	18	13	
	ININ10:ININ11	39	13	30	
	AR123TMB:ININ1	23	45	42	
	Orange	TC3P2:TC3P3	35	0	49
		TC3P3:TC3P4	36	0	44
		TC3P5:T124TMB	51	0	39
		TC3P2:T124TMB	63	28	51
		T124TMB:T123TMB	59	8	40
		TC5P1:TC5P2	46	0	45
TC1PNA1:TC1PNA2		43	4	53	
AREB:ARXMP		62	1	64	
ARXMP:ARXO		61	30	63	
ARC3P5:AR124TMB		60	5	48	
Gray	ARC3P2:AR124TMB	54	16	59	
	AR124TMB:AR123TMB	57	6	47	
	ARC4G1P1:ARC4G1P2	49	11	31	
	ININ6:ININ7	40	22	33	
	PNAC1PNA1:PNAC1PNA2	38	2	60	
	T123TMB:TIN1	55	38	29	
	TC4G3P1:TC4G3P2	41	36	27	
	ALKC9:ALKDIS9	58	34	25	
	ALKISDS1:ALKISDS2	45	35	10	
	ALKISDS4:ALKC11	47	39	28	
Red	ARC5P4:ARC5P5	50	47	17	
	ARC5P5:ARC5P6	33	33	21	
	ARC5P6:ARC5P7	34	46	6	
	ARC3P5:ALKISO2	44	41	23	
	ALKC10:ALKDIS11	*	0	61	
	ARC3P3:ARC3P4	56	42	54	
	ININ2:ININ3	31	31	41	

20) of the samples previously determined not to contain gasoline plotted in the negative region. The remaining five samples plotted into the complex region, meaning that they may be reported as either containing gasoline or not containing gasoline. The final determination is based on the evaluation by the examiner and should be justified in the case record documentation.

The original determinations were other (non-gasoline) Ignitable liquid identification, gasoline identification, or no ignitable liquid



**Fig. 10.** Graph of total points attained by gasoline control and negative matrix samples. This graph depicts the separation of the samples using the established point system and was made using Prism 8 software.

identification. An “agreement” between the original determination and the results of the sufficiency method was designated as any result that was deemed negative or as a non-gasoline other ignitable liquid and fell into the negative region or was a gasoline identification that fell into the non-complex region. This left five samples that fell into the complex region of the sufficiency graph. The examiner’s subjective binary designation of “complex” or “non-complex” was included to better characterize samples that fell in the complex yellow region of the graph. By this method, four of the five samples that fell into the complex region were designated as complex, and the remaining sample was designated as non-complex.

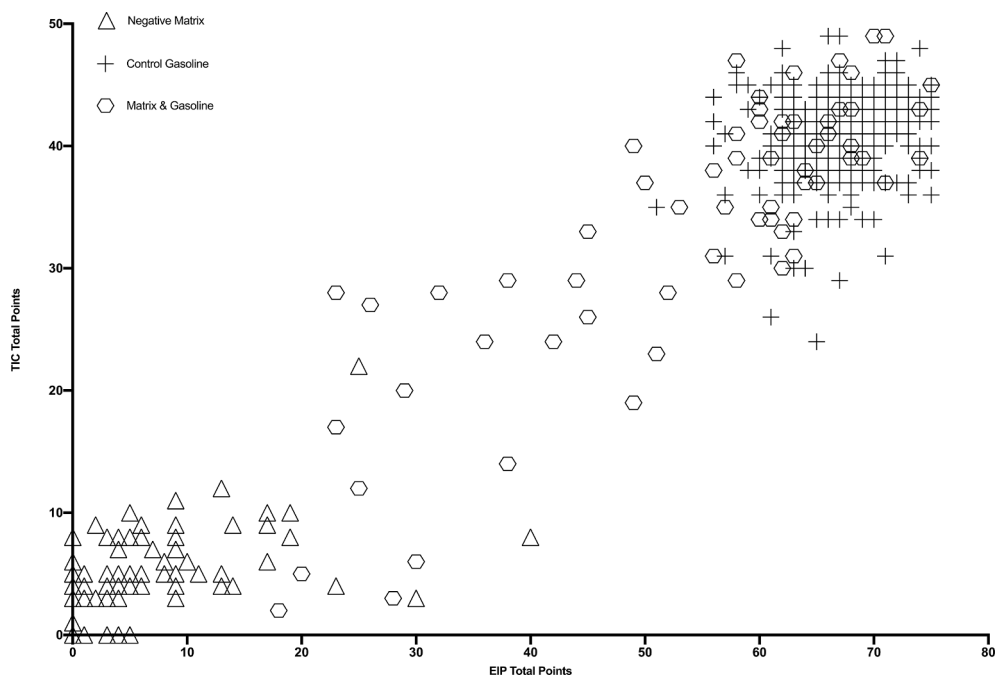
The original reported conclusions and the sufficiency determinations are consistent in their outcome. Taken together, the 30 processed and plotted Previously Determined Data Files represent a continuum of data ranging in complexity, which highlights the utility of the sufficiency graph as a support tool for case-like sample determinations and further bolsters the efficacy of the line placements.

#### 3.4.4. Reproducibility evaluation

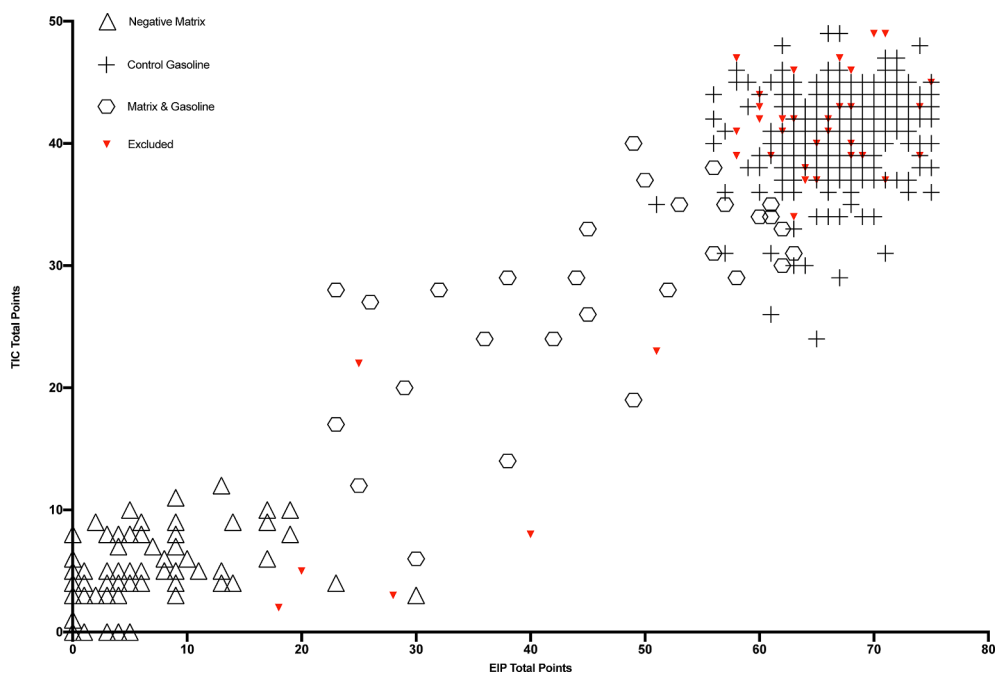
Each sample was processed by six staff members from the Virginia Department of Forensic Science. Three of these individuals were involved in the method development and three were not. The results of the first attempt prior to training are shown in Fig. 18.

The graphical representation of the data on the sufficiency graph (Fig. 18) shows a lack of consistency and little reproducibility in the final point determinations between the examiners. Therefore, several data comparisons were performed to elucidate the source of the variation between examiners. In general, the data comparison of each examiner’s results revealed the source of the variability was likely from a lack of understanding in how to properly apply their existing expertise to the novel method. More specifically, the comparisons revealed that variability occurred due to differences in background subtraction and subsequent manual tabulations, the presence of co-elutions effecting peak inclusion, the abundance of the peaks, differences in integration thresholds, data entry errors, and evaluating the data based only on retention times and not confirming the pattern and mass spectra. On this basis, guidance was created and implemented via a web-based training to guide the examiners’ analysis process within the novel method. The drafted guidance is outlined below in Table 11.

Following the training and implementation of the above guidance, the examiners were asked to reevaluate the same samples. The request to reevaluate the same samples allowed the examiners to focus on the application of the newly implemented training rather than navigate a new set of samples. The updated scores for the samples were then plotted to see how the training affected the inter-examiner reproducibility



**Fig. 11.** Graph of total points attained by gasoline control samples, negative matrix samples, and matrix with gasoline samples. This graph depicts the separation of the samples using the established point system as well as the continuum of data from the matrix with gasoline samples. This graph was made using Prism 8 software.



**Fig. 12.** Graph of gasoline control samples, negative matrix samples, and matrix with gasoline samples used for LDA analysis for decision line placement. The data points excluded from LDA analysis are marked. This graph was made using Prism 8 software.

(Fig. 19).

The graphical representation of the data on the sufficiency graph (Fig. 19) shows a greater degree of consistency and more reproducibility following training. The majority of the examiners were able to utilize the training and immediately generate consistent results. To confirm that the improvement was based on the training and not familiarity with the samples, three new samples (one negative, one control gasoline, and one matrix with gasoline) were given to the examiners to analyze using the sufficiency method. The results for the second iteration are shown in Fig. 20. As an example, the TIC for Unknown 6, which scored in the

complex region, is included as Fig. 21.

There are six data points per sample, represented in Fig. 20, though less data points per sample are visible due to overlap. The points have generally proven to be reproducible and the multiple iterations allowed for a better understanding of the areas of the analysis where training is required.

#### 4. Conclusions

Gas chromatography-mass spectrometry is generally considered the



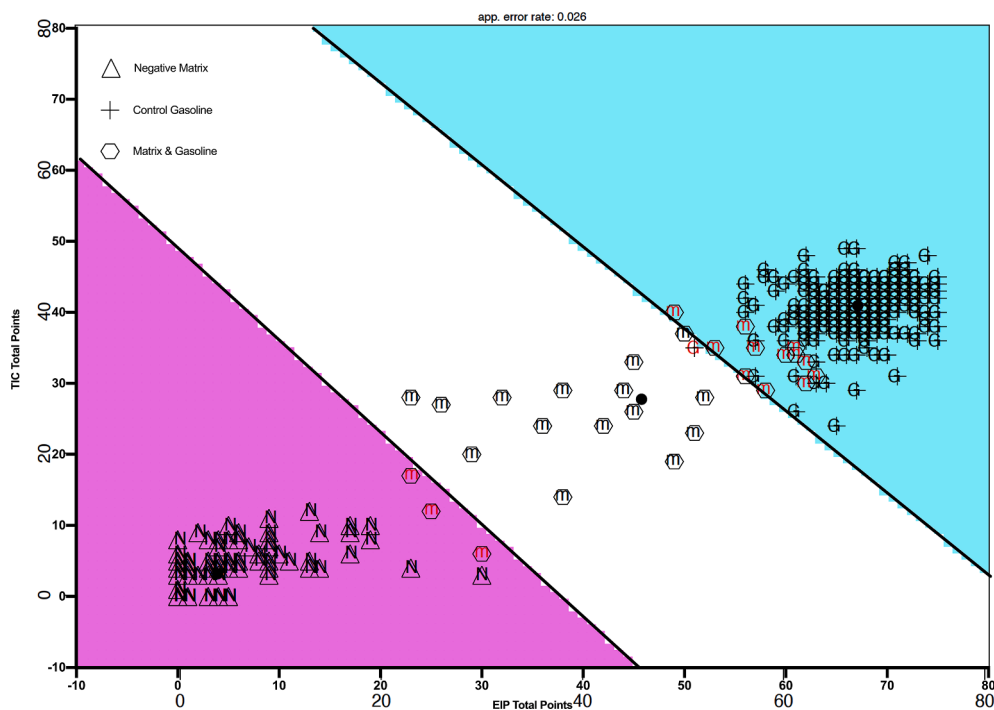


Fig. 13. Line mapping the R-based partition plot in using Prism 8.

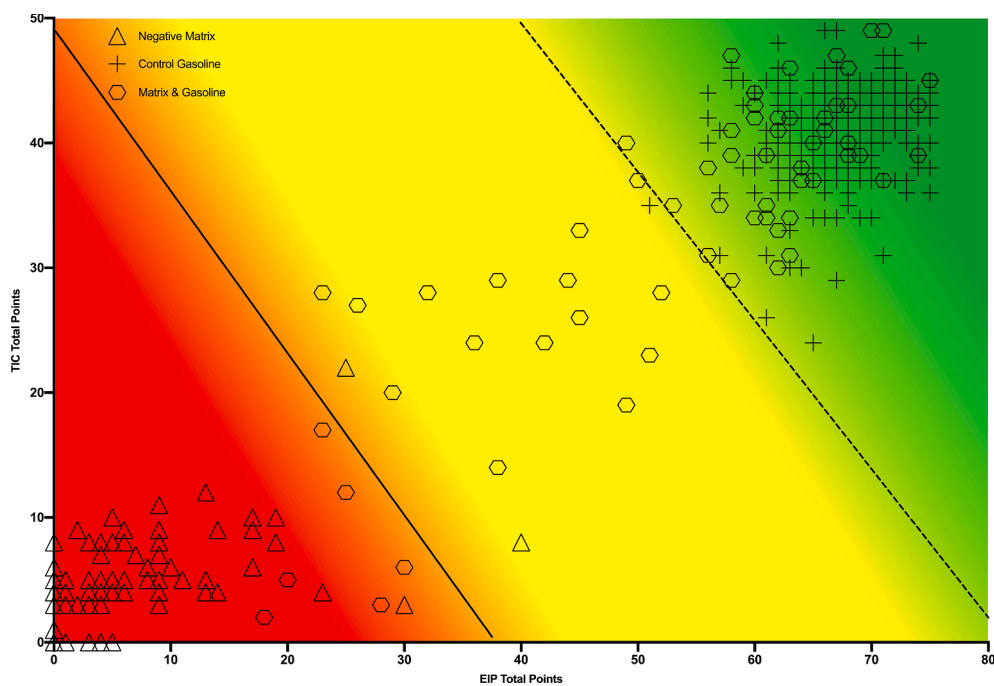


Fig. 14. Sufficiency graph with decision lines and the gasoline control samples, negative matrix samples, and matrix with gasoline samples plotted. This graph was made using Prism 8 software.

gold-standard for organic compound identification. However, the application of GC-MS to fire debris analysis is a chromatographic pattern matching technique where the appearance of peak groupings are visually compared between unknown samples and reference ignitable liquids. Since many of the compounds that make up petroleum products can also be produced by the thermal degradation of common matrices, the identification of any given compound or even groups of compounds is not sufficient for the identification of an ignitable liquid. The visual comparison of peak patterns currently used is generally sufficient for

recognizing ignitable liquids in concentrated samples and samples with non-complex matrices. However, when complex matrices are present and when the concentration of possible ignitable liquids results in chromatographic features in comparable orders of magnitude to that of the matrix, ignitable liquid identification becomes increasingly subjective. The methodology proposed in this study provides for a statistically supported mechanism to evaluate complex data and reduce the subjectivity of gasoline identification. By using closely eluting peak pair ratios, this method improves on the current pattern recognition methodology

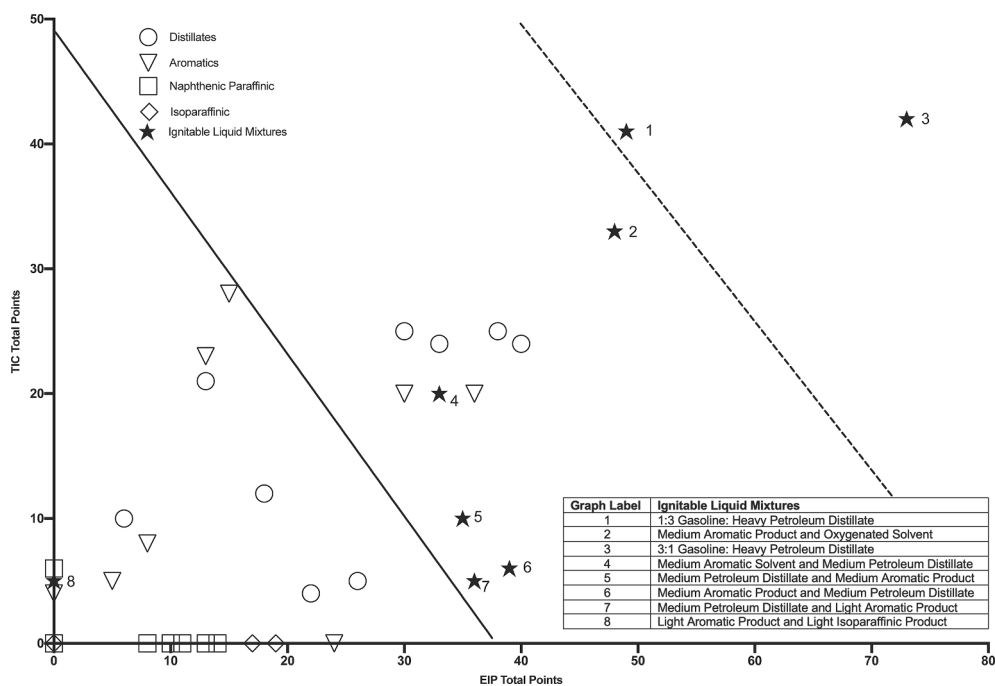


Fig. 15. Ignitable liquid classifications other than gasoline and Ignitable liquid mixtures plotted on the sufficiency graph.

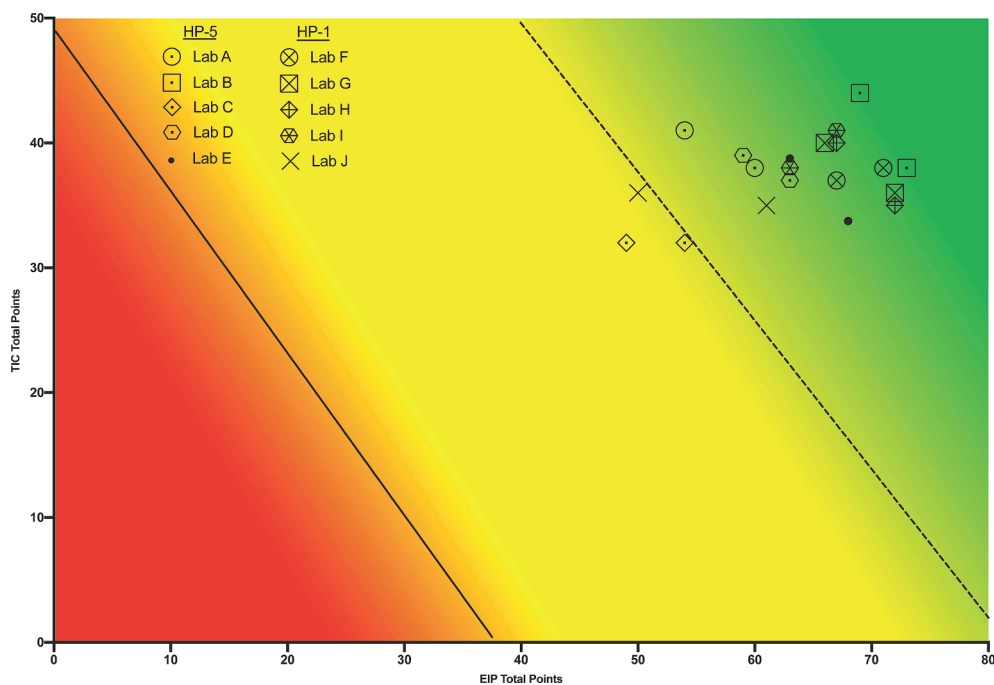


Fig. 16. Other laboratory methods on the sufficiency graph.

without necessitating changes to a laboratory's current instrumental acquisition methods.

Although alkylbenzene peak patterns, especially C3 and C4 alkylbenzenes, are most commonly employed as chromatographic features of interest for gasoline, this project objectively assessed their significance in relation to complex matrices. The study found that C3 alkylbenzenes, historically referred to as the "castle group" and considered critical to gasoline identification, did not provide statistically significant support for identification as compared to other peak patterns. The indane, C4 alkylbenzene and 2,3,4-trimethylbenzene:toluene groupings were more distinctive; however, no single peak grouping was found to be unique or

solely indicative of gasoline. The product of this analysis as applied to an unknown sample are plot values developed from the TIC and EIPs. These plot values graphically demonstrate the totality of the data present to support the identification of gasoline.

The sufficiency graph with decision lines was built and validated using a data-based approach to allow for an objective, reproducible visual representation of the quantity of data available to support the identification of gasoline in unknown samples. Although the basis of the finalized sufficiency template is a statistically supported, predictive model, it does not necessarily dictate a conclusion. Rather, the decision lines allow for the rapid identification of samples that have significant

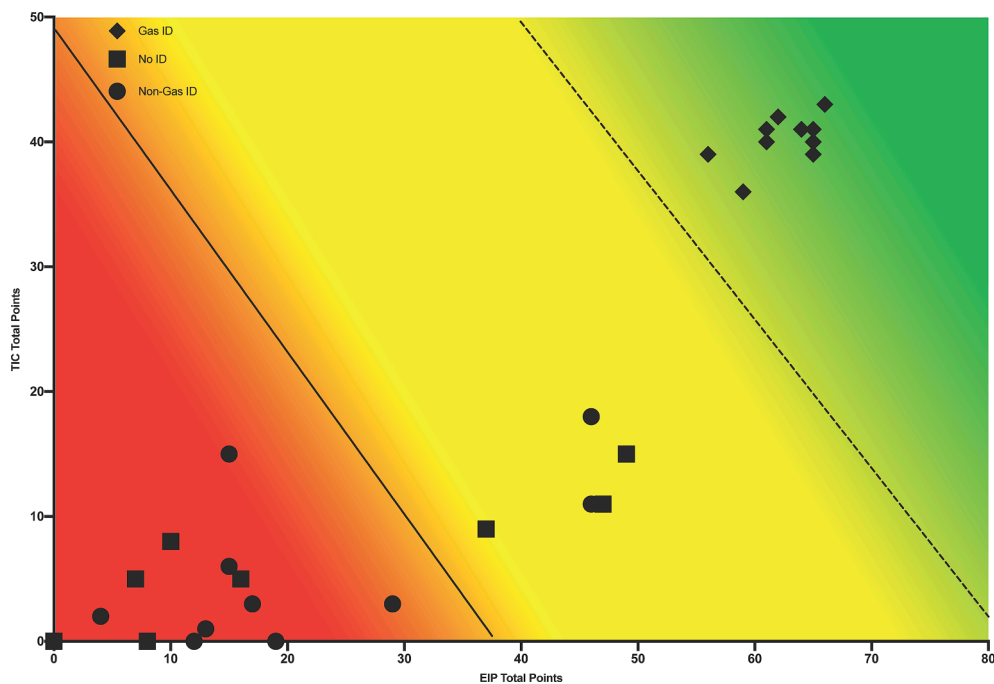


Fig. 17. Previously determined data files plotted on the sufficiency graph. Gas ID shows those where gasoline was previously identified, No ID shows data where no ignitable liquids were previously identified, and Non-Gas ID shows data where ignitable liquids other than gasoline were identified.

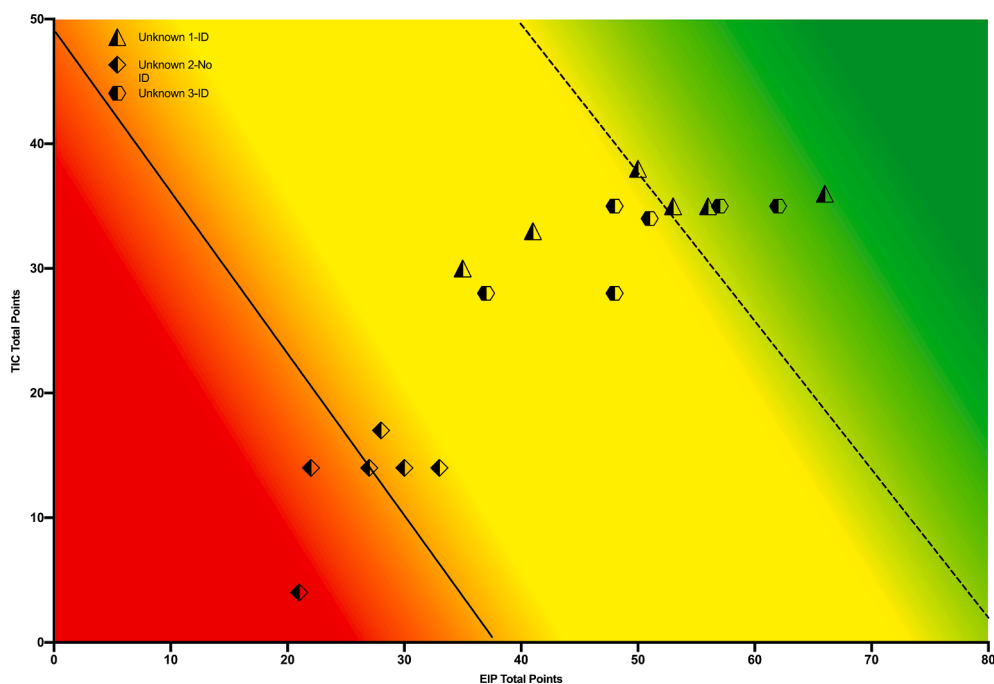


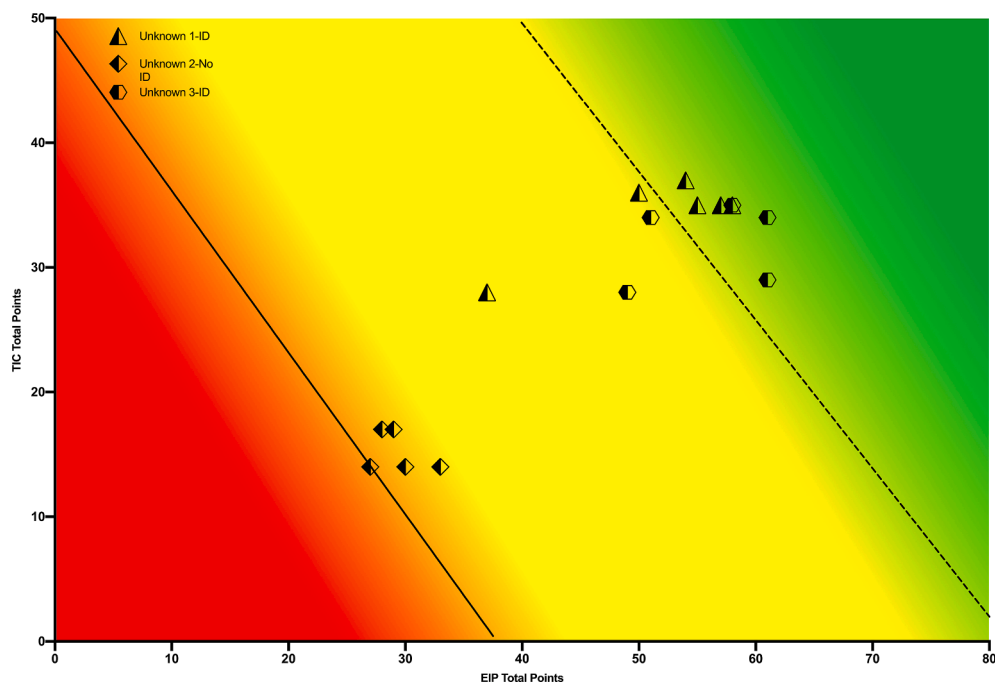
Fig. 18. First reproducibility evaluation; pre-training.

support for the identification of gasoline and those that do not have enough support to pursue gasoline. The sufficiency graph also informs the examiner, the reviewer, and potentially the trier of fact if a sample is complex with regard to the information available to support a gasoline identification. The decision regarding the identification of gasoline in these complex samples is not dictated by the method, but dependent on the interpretation and documentation by the examiner. The finalized sufficiency graph with plotted sample points is intended to become a part of the case record along with the documented decision made by the experienced examiner.

Currently, the consensus standard for identification and classification of ignitable liquids and ignitable liquid residues is *ASTM E1618-19 Standard Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry* [4]. The guidance in this standard is limited to generalities about “the matching of the sample chromatogram with a reference ignitable liquid chromatogram obtained under similar conditions, noting points of correlation or similarities” [4]. The document goes further to describe “Criteria for the Identification of Gasoline” which include brief pattern illustrations and hydrocarbon class characteristics [4]. ASTM E1618 lacks definitive guidance

**Table 11**  
Guidance for using the sufficiency method.

	Guidance	Explanation
Manual Integration	Manual integrations need to be background subtracted from an area in the baseline at the level of the integration line.  Check that the manual integration of the target peak is accurate by confirming that the manually tabulated abundance is close to an automatically tabulated abundance of a nearby peak with a similar height.  Manual tabulations in the TIC should include the sum of all background subtracted ions. Manual tabulations in the EIPs should include the sum of only the background subtracted ions of interest.	Peaks that do not automatically integrate, but are clearly present based on pattern and mass spectra, should have their abundance manually tabulated. To do so consistently and in comparison with the integrated peaks, the manual integrations must be background subtracted in a similar and consistent fashion. Peaks that do not automatically integrate, but are present based on pattern and mass spectra, should have their manually tabulated abundance verified by comparing it with the automatically tabulated abundance of a nearby peak with similar height. This confirms that the abundance is appropriate. Summing all background subtracted ions for the TIC, and only the ions of interest for EIP mirrors the automated peak height tabulation.
Co-Elutions	Look for co-elutions by checking the mass spectra; confirm that the ions of interest are present in similar ratios to those of the reference gasoline for a given peak. If present with a co-elution, the peaks is included.  Co-elutions in the EIPs have less of an effect on the results than co-elutions in the TIC.	Although pattern matching should be used as a first step, peaks of interest may co-elute with other compounds present in the matrix. Therefore, it is important to confirm the appropriate mass spectra is present within the peak. Co-elutions are more commonly observed in the Alkane EIP. Peaks of interest may co-elute with other compounds present in the matrix. However, the EIPs only display the abundance for the ions of interest, while the TIC displays the abundance of all ions present. Therefore, a co-elution observed in the TIC may not be observed in the EIP.
Selecting Peaks	Compare the retention time, overall pattern, and mass spectra of an unknown to those of a reference sample. Peaks that do not have an apex should not be selected.  On peaks of interest, integration lines need to be flat and not angled.	Overall pattern, retention time, and mass spectra should be compared and considered when selecting peaks. If a shoulder or partially resolved peak is one of interest, it needs to have an apex to be selected. As much as possible, it is important that the integration line not be angled as this will affect the abundance of the peak. This can often be corrected by changing the integration parameters prior to generating the percent report. Peaks that constitute peak pairs should have a similarly placed integration line.
Data Entry Errors	Confirm that there are not data entry errors in the automated processing tool.	It is important to check for examiner data entry errors prior to making final determinations as errantly missing or incorrect values can affect the outcome.



**Fig. 19.** First reproducibility evaluation; post-training.

for interpreting data when complex matrices are present that may alter or mimic patterns typified in gasoline. The standard does not have a mechanism to evaluate the strength of a possible agreement between the unknown sample and a reference ignitable liquid. The result is subjectivity potentially causing two analysts to reach different conclusions regarding the presence or absence of gasoline in a sample. This study fills those gaps with a method that is intuitive to explain and is relevant to fire debris analysts as an extension of what they are doing in the lab; especially when compared to other methodologies, like PCA-LDA. By

applying a statistical method based upon peak pair ratios, the level of subjectivity is greatly reduced and the strength of a potential association between the unknown sample and a reference ignitable liquid can be easily assessed.

The study was limited to gasoline samples up to 90% evaporated. Further evaporation levels, beyond 90% evaporated, would need additional study as some of the peak pair ratios studied, such as toluene, C2 and C3 alkylbenzenes, and some C4 alkylbenzenes, are lost in highly evaporated samples [38]. The relative peak heights of compounds with

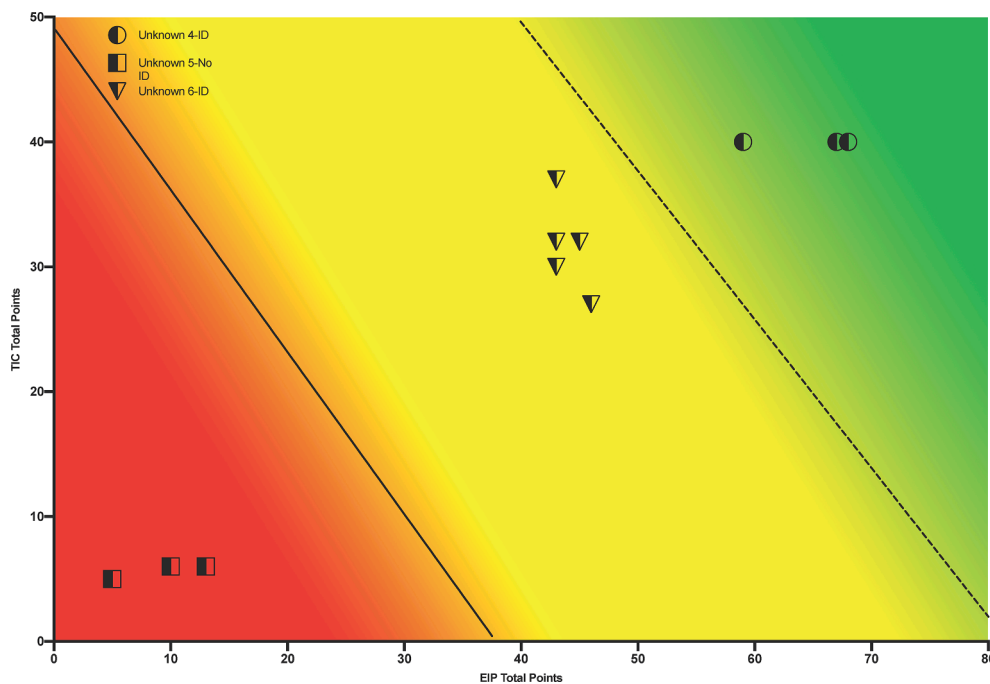


Fig. 20. Second reproducibility evaluation.

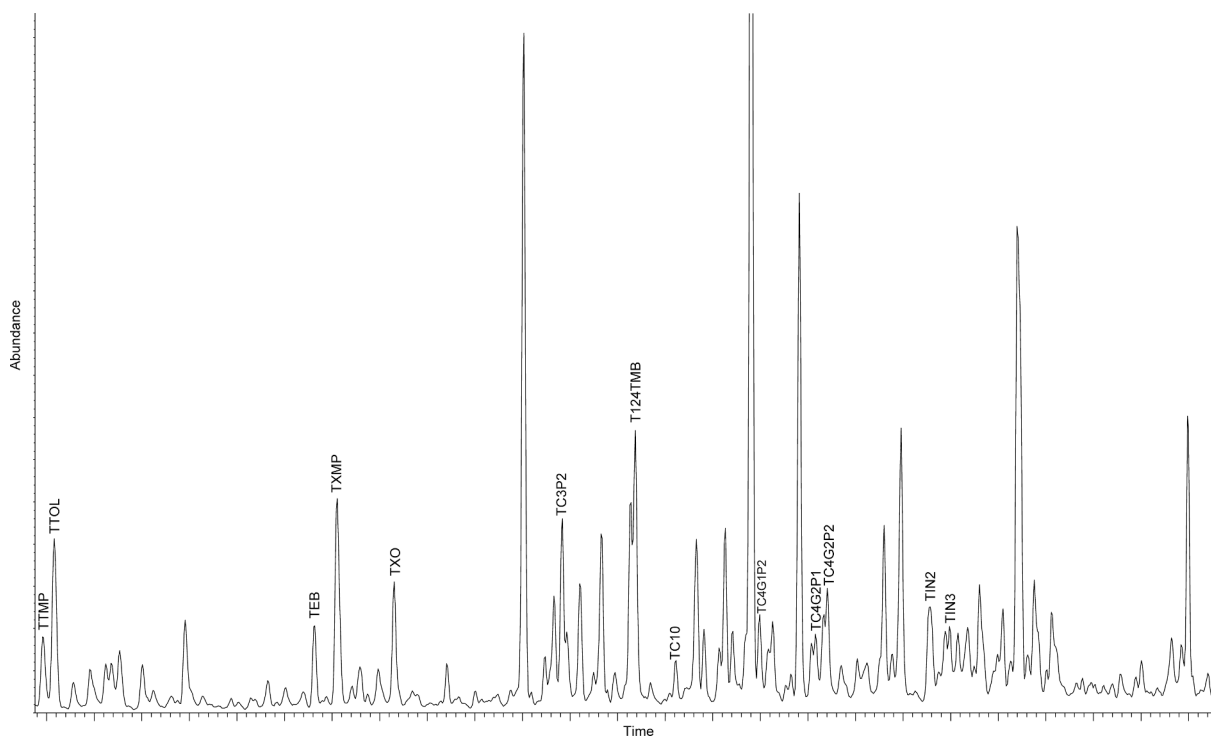


Fig. 21. TIC for Unknown 6 of the reproducibility evaluation. Select peaks are labeled for reference.

higher boiling points that are not present at a significant abundance in the samples studied may have increased relative abundance with these further evaporations and would be suitable for a similar statistical analysis.

The results of this study have been applied to the development of a sufficiency graph with decision lines to demonstrate the sufficiency of the data for the identification of gasoline to further strengthen the data interpretation process and provide transparent documentation. The continuation of these research efforts will include a repetition of the

developed system for other ignitable liquid classifications and the standardization of methods for enhanced documentation and verification. Additionally, since PCA-LDA has also been a commonly used method for dimension reduction and classification, a future topic is to explore methods including PCA-LDA and directly compare their classification performance with the method in this paper. The objective of this cumulative study, including its application and implementation, is to make the fire debris analysis process more standard, objective, and transparent by establishing a validated method with quantitative

measures that include the implementation of documentation methodology and verification.

### CRedit authorship contribution statement

**Brenda Christy**: : Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Supervision, Funding acquisition. **Kelsey Winters**: Methodology, Validation, Investigation, Resources, Writing - review & editing. **Alexandria Rosshiem**: Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing. **Reta Newman**: Methodology, Investigation, Resources, Writing - review & editing. **Larry Tang**: Methodology, Formal analysis, Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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