Document Title:	**Fire Debris Interpretation Using Quantitative Measures of Chromatographic Features in Medium-Range Ignitable Liquids and the Use of Graphical Display to Demonstrate Data Sufficiency**
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Document Number:	**311972**
Date Received:	**June 2026**
Award Number:	**15PNIJ-22-GG-03577-SLFO**

FIRE DEBRIS INTERPRETATION USING QUANTITATIVE MEASURES OF CHROMATOGRAPHIC FEATURES IN MEDIUM RANGE IGNITABLE LIQUIDS AND THE USE OF GRAPHICAL DISPLAY TO DEMONSTRATE DATA SUFFICIENCY

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Award Number:

15PNIJ-22-GG-03577-SLFO

Project Period:

January 1, 2023 – December 31, 2025

Award Amount:

$141,921

PROJECT SUMMARY

Abstract

The analytical process for identifying ignitable liquids is based on fundamental chemical properties; however, the current interpretation of these properties in chromatographic data relies on subjective pattern recognition techniques. The subjectivity of these pattern recognition techniques increases with the presence of complex matrix contributions. To make the fire debris interpretation process more standardized and objective, a method was developed 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 chromatogram and extracted ion profiles. Medium petroleum products were examined for suitability for study, and medium petroleum distillates and medium isoparaffinic products were determined to be suitable. Statistical analysis was conducted on the selected chromatographic peak pair ratios to determine the variation observed for each ratio 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 the features. When summed and used as plot values, the cumulative scores generally graphically display the separation of the known ignitable liquid 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 identification. In theory the sufficiency graph also identifies the "gray" area where analysts are more likely to form differing opinions. The peak pair ratios present in the petroleum products were not frequently present in the negative matrix samples. Due to the limited overlap, unlike the previous study on gasoline, the gray areas for the studied medium petroleum products were not defined. The methodologies

developed can be used as a step toward a consistent documentation process that displays the data present to support an identification, which ensures greater transparency in fire debris examinations and comparisons.

Goals and Objectives

The project was completed in two phases:

1) A data interpretation process was developed and validated for the identification of medium petroleum products.

2) This process was used as part of an analysis method that facilitates documentation of features used by an examiner to formulate a conclusion.

The goal of this project was to develop and validate a data interpretation method for medium petroleum products that is transparent and can be applied to normalize interpretation and strengthen the science of fire debris analysis.

The project had the following objectives:

- Objective 1 – Determine and quantify significant identifying criteria for medium petroleum products including distillates, isoparaffinic products, naphthenic paraffinic products, aromatic solvents and highly evaporated gasoline by using statistical measures to evaluate the uniqueness and consistency of closely eluting peak pair ratios.

- Objective 2 – Based on the data, create a sufficiency graph (or graphs) with decision curves based upon key diagnostic peak pair ratios in the Total Ion Chromatogram (TIC) and Extracted Ion Profiles (EIPs).
- Objective 3 – Evaluate the process with samples extracted from complex matrices with and without the addition of medium petroleum products to evaluate both the robustness of target peak pair ratios and the efficacy of differentiating those components from those generated by the pyrolysis and thermal degradation of complex fire debris.
- Objective 4 – Evaluate additional statistical data processing such as Receiver Operating Characteristic (ROC) curves to develop more robust decision point standards for identification and thus further minimize interpretation variations among analysts.
- Objective 5 – Evaluate the developed process in relation to current methodologies through comparison of analysis by experienced forensic analysts using contemporary methods of comparison and the methods developed in this process.

Research Question

Can we establish a statistically supported sufficiency model for medium petroleum products?

Summary of Project Design and Methods

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. Following a foundational study establishing a method for determining the sufficiency of a sample for gasoline identification, (2018-DU-BX-0174) the process was repeated with a focus on medium petroleum products. After gasoline, medium petroleum products are typically the most identified

ignitable liquids in fire debris samples. Medium petroleum products are those with major chromatographic peaks present between approximately n-C8 and n-C13. The classifications of medium petroleum products include petroleum distillates, isoparaffinic products, naphthenic paraffinic products, and aromatic products. While evaluating marketed products for this study, it was determined that the only classifications with enough products for meaningful statistical comparison were medium petroleum distillates (MPDs) and medium isoparaffinic products (MIPs). The previously completed gasoline-based study was limited to samples that were no more than 90% evaporated, so an additional area of study was highly evaporated gasoline samples (95-99% evaporated) as these also fall into the medium chromatographic range.

This study sought to determine chromatographic characteristics of MPDs and MIPs that can statistically quantify the comparison, which would be particularly useful in unknown samples with complex matrices. First, peaks from Gas Chromatogram-Mass Spectrometer (GC-MS) data were selected from known MPD and MIP samples for the collection of peak height values across evaporation levels (whole, 25%, 50%, 75%, and 90%) and varying chromatographic methods. These peak height values were used to calculate peak pair ratios by dividing the height of the first eluting peak by the height of the second eluting peak. Peak pair ratios were selected that are closely eluting to minimize the effect of evaporation and chromatographic method influence on the peak pair. The peaks evaluated are represented on the peak maps in Figures 1-5. The total number of peaks included in the analysis and peak height ratios studied are outlined in Tables 1-4. The chromatographic methods used are detailed in Table 5. The peaks included in the study for MPDs were from the TIC, alkanes EIP, cycloalkanes EIP, aromatic EIP, and indane EIP. As the study progressed, the aromatic EIP and indane EIP were eliminated as they were only present in some of the MPD products. The compounds composing MIP products are present in the TIC

and only represented in the alkanes EIP. Therefore, only the TIC and alkanes EIP were studied for MIP products.

Figure 1: Medium Petroleum Distillate TIC Peak Map

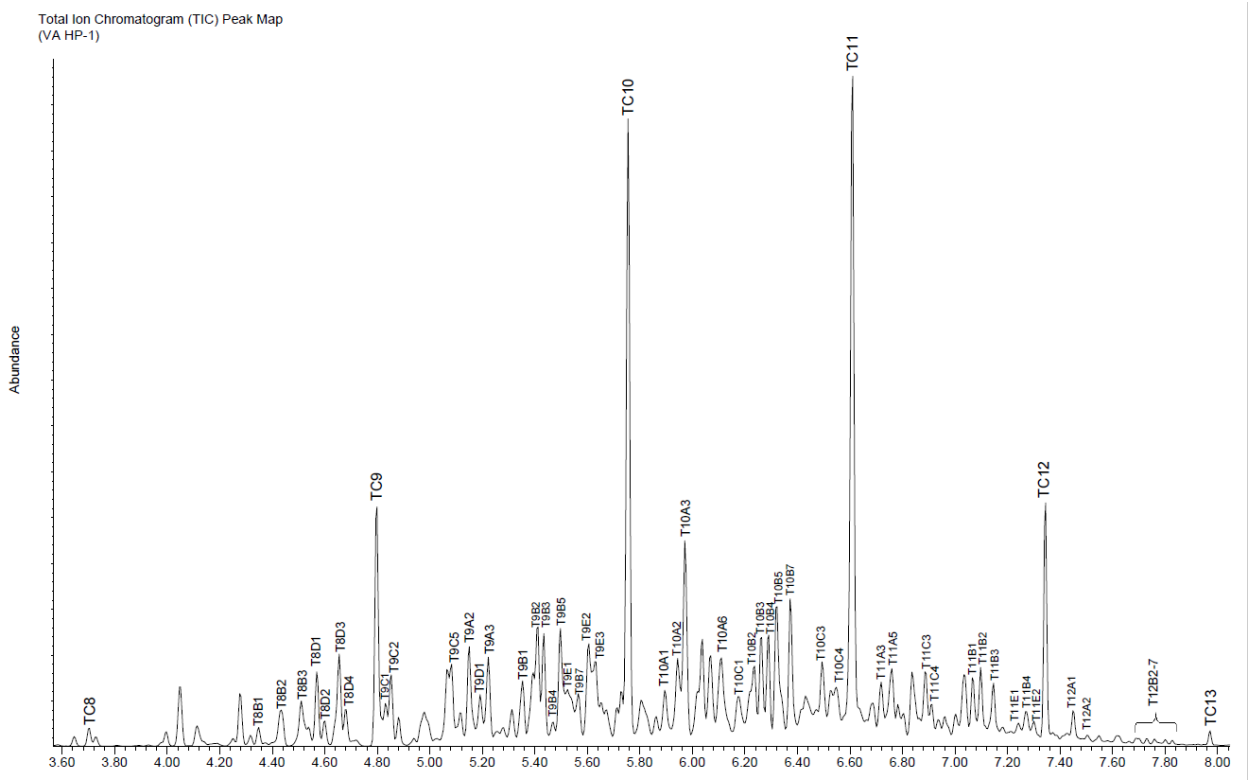


Figure 2: Medium Petroleum Distillate Alkanes EIP Peak Map

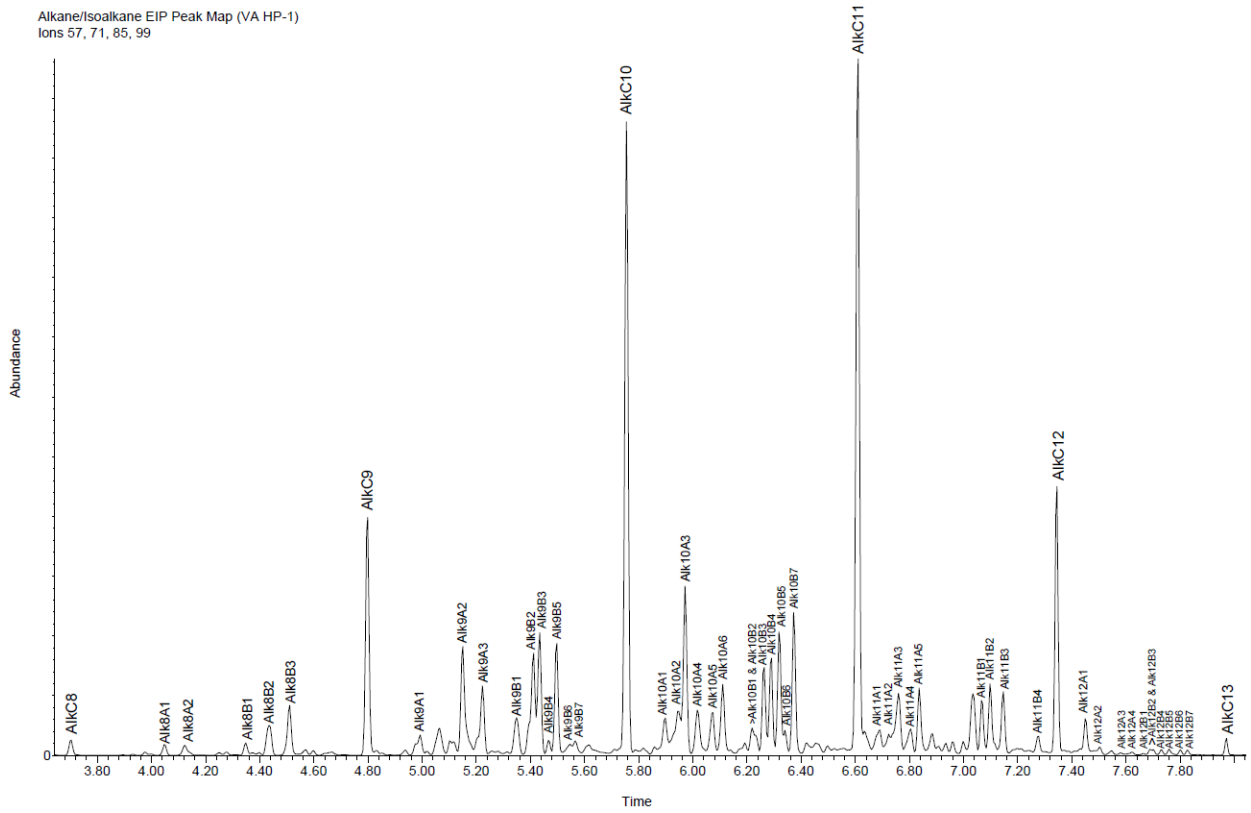


Figure 3: Medium Petroleum Distillate Cycloalkanes EIP Peak Map

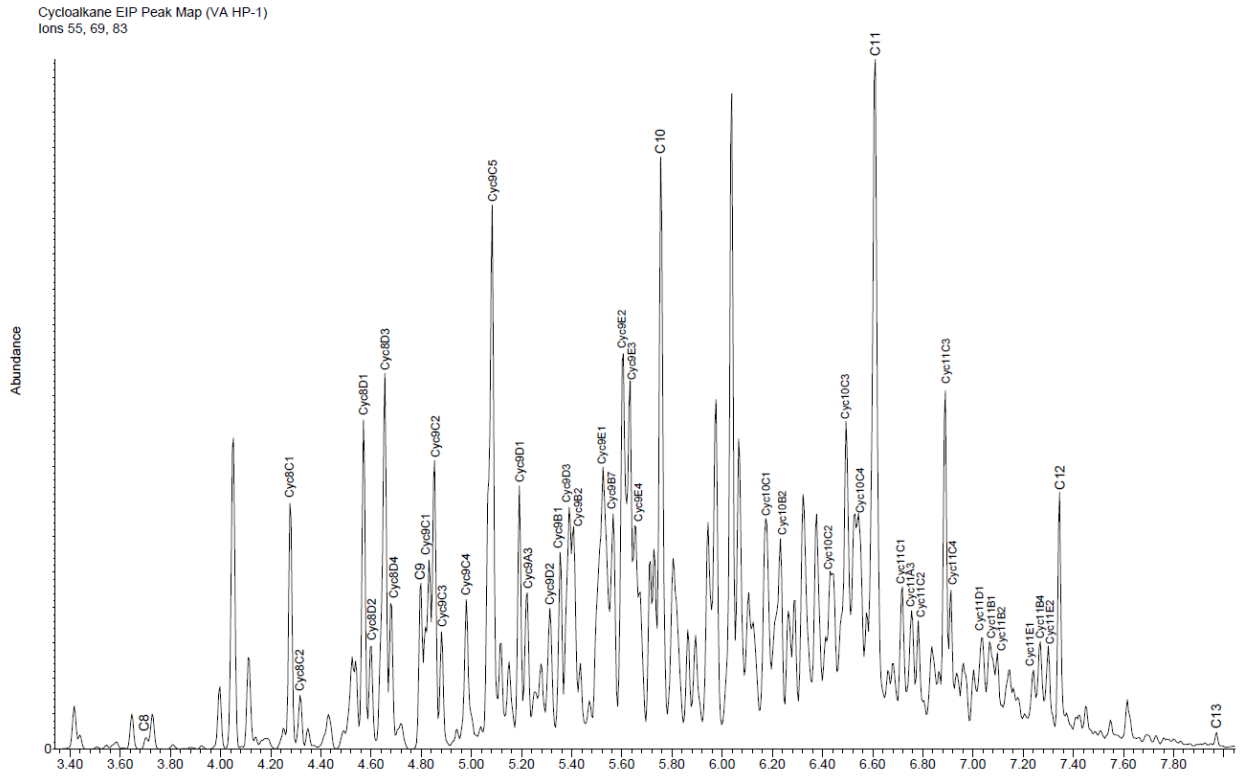


Figure 4: Medium Isoparaffinic Product TIC Peak Map

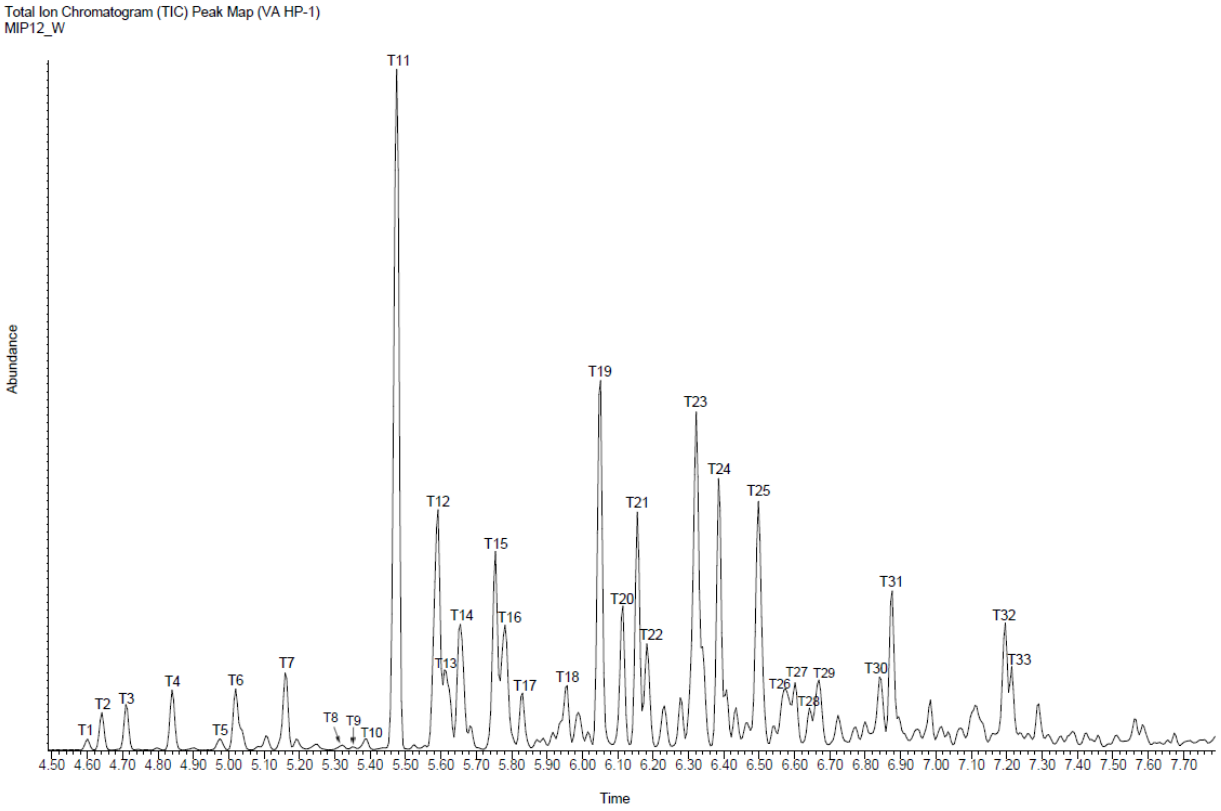


Figure 5: Medium Isoparaffinic Product Alkanes EIP Peak Map

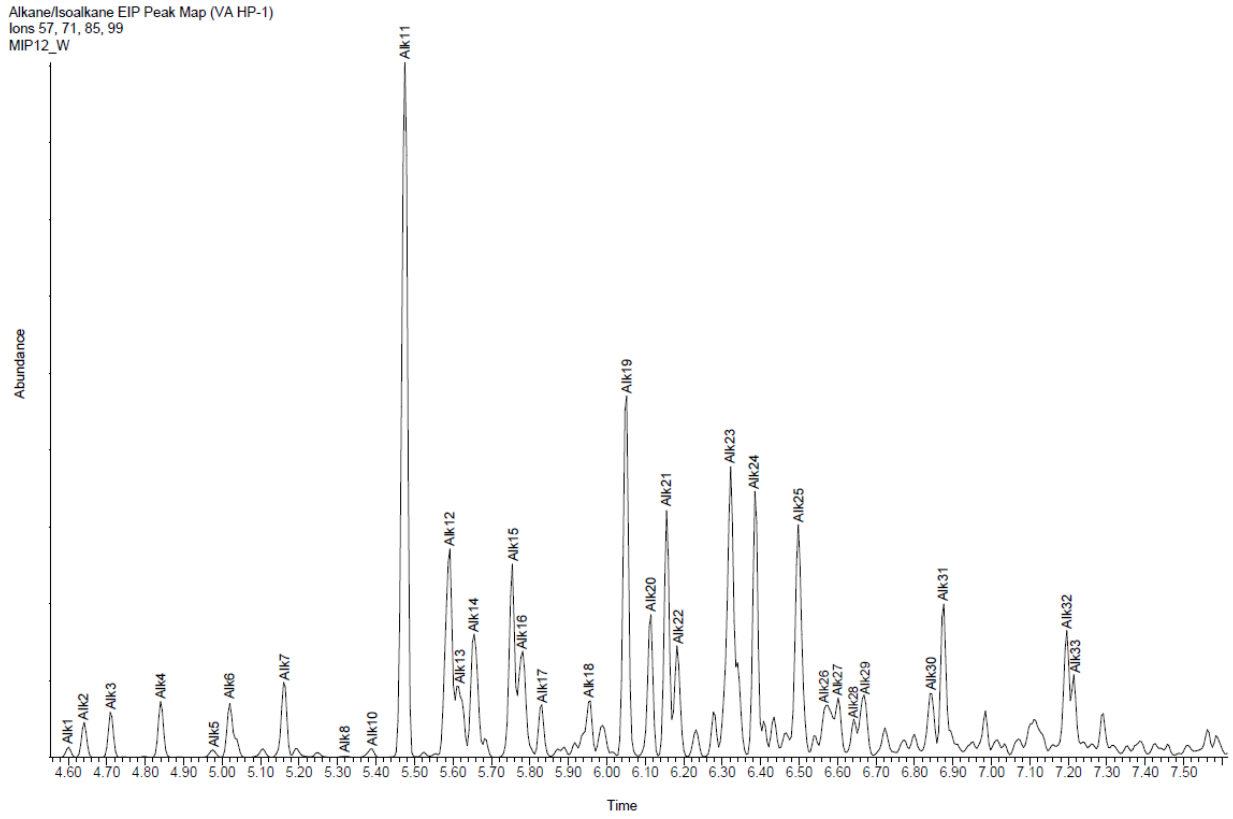


Table 1. Summary of the Medium Petroleum Distillate Chromatographic Features of Interest

Data Display	**Ions used**	**Number of peak heights determined**	**Number of ratios calculated for statistical analysis**
Total Ion Chromatogram (TIC)	All used in methods	57	36
Alkanes EIP	57, 71, 85, 99	52	35
Cycloalkanes EIP	55, 69, 83	43	23
Aromatic EIP	91, 105, 119, 133	25	17
Indane EIP	117, 118, 131, 132	11	7

Table 2. Summary of the Medium Isoparaffinic Chromatographic Features of Interest

Data Display	**Ions used**	**Number of peak heights determined**	**Number of ratios calculated for statistical analysis**
Total Ion Chromatogram (TIC)	All used in methods	36	33
Alkanes EIP	57, 71, 85, 99	32	26

Table 3. Peak Height Ratios Studied for MPDs

TIC Ratios	**Alkane EIP Ratios**	**Cycloalkane EIP Ratios**	**Aromatic and Indane EIP Ratios**
T8B1:T8B2	Alk8A1:Alk8A2	Cyc8C1:Cyc8C2	ArEB:ArXMP
T8B2:T8B3	Alk8B1:Alk8B2	Cyc8D1:Cyc8D2	ArXMP:ArXO
T8D1:T8D2	Alk8B2:Alk8B3	Cyc8D1:Cyc8D3	ArC3P1:ArC3P2
T8D3:T8D4	Alk8B3:AlkC9	Cyc8D3:Cyc8D4	ArC3P2:ArC3P3
TC9:T9C1	AlkC9:Alk9A1	Cyc9C1:Cyc9C2	ArC3P3:ArC3P4
TC9:T9C2	AlkC9:Alk9A2	Cyc9C2:Cyc9C3	ArC3P4:ArC3P5
T9C1:T9C2	Alk9A2:Alk9A3	Cyc9C3:Cyc9C4	ArC3P5:Ar124TMB
T9C5:T9A2	Alk9B1:Alk9B2	Cyc9C4:Cyc9C5	ArC3P2:Ar124TMB
T9D1:T9A3	Alk9B2:Alk9B3	Cyc9D1:Cyc9A3	Ar124TMB:Ar123TMB
T9B1:T9B2	Alk9B4:Alk9B5	Cyc9D2:Cyc9B1	ArC4G1P1:ArC4G1P2
T9B3:T9B5	Alk9B3:Alk9B5	Cyc9D3:Cyc9B2	ArC4G1P2:ArC4G1P3
T9B4:T9B5	Alk9B5:AlkC10	Cyc9E1:Cyc9E2	ArC4G1P3:ArC4G1P4
T9E2:T9E3	AlkC10:Alk10A3	Cyc9E2:Cyc9E3	ArC4G2P1:ArC4G2P2
TC10:T10A3	Alk10A1:Alk10A2	Cyc9E3:Cyc9E4	ArC4G3P1:ArC4G3P2
T10A1:T10A2	Alk10A2:Alk10A3	Cyc10C1:Cyc10B2	ArC5P3:ArC5P4
T10A6:T10C1	Alk10A4:Alk10A5	Cyc10C2:Cyc10C3	ArC5P5:ArC5P6
T10C1:T10B2	Alk10A5:Alk10A6	Cyc10C3:Cyc10C4	ArC5P7:ArC5P2
T10B3:T10B4	Alk10B1:Alk10B2	Cyc11C1:Cyc11A3	IN2:IN3
T10B4:T10B5	Alk10B3:Alk10B4	Cyc11A3:Cyc11C2	IN4:IN5
T10B5:T10B7	Alk10B5:Alk10B6	Cyc11C3:Cyc11C4	IN5:IN6
T10B7:TC11	Alk10B6:Alk10B7	Cyc11D1:Cyc11B1	IN6:IN7
T10C3:T10C4	Alk10B7:AlkC11	Cyc11B1:Cyc11B2	IN8:IN9
T11A3:T11A5	Alk11A1:Alk11A2	Cyc11E1:Cyc11B4	IN9:IN10
T11C3:T11C4	Alk11A2:Alk11A3	Cyc11B4:Cyc11E2	IN10:IN11
T11B1:T11B2	Alk11A4:Alk11A5		
T11B2:T11B3	Alk11B1:Alk11B2		
T11E1:T11B4	Alk11B2:Alk11B3		
T11B4:T11E2	Alk11B4:AlkC12		

TC12:T12A1	AlkC12:Alk12A1
T12A1:T12A2	Alk12A1:Alk12A2
T12B2:T12B3	Alk12A3:Alk12A4
T12B3:T12B4	Alk12A4:Alk12B1
T12B5:T12B6	Alk12B2:Alk12B3
T12B6:T12B7	Alk12B4:Alk12B5
T12B7:TC13	Alk12B6:Alk12B7

Table 4. Peak Height Ratios Studied for MIPs

TIC Ratios	**Alkane EIP Ratios**
T1:T2	Alk1:Alk2
T2:T3	Alk2:Alk3
T3:T4	Alk3:Alk4
T5:T6	Alk5:Alk6
T6:T7	Alk6:Alk7
T8:T9	Alk8:Alk10
T8:T10	Alk10:Alk11
T10:T11	Alk11:Alk12
T11:T12	Alk12:Alk13
T12:T13	Alk13:Alk14
T13:T14	Alk14:Alk15
T14:T15	Alk15:Alk16
T15:T16	Alk17:Alk18
T17:T18	Alk19:Alk20
T19:T20	Alk21:Alk22
T21:T22	Alk21:Alk23
T21:T23	Alk23:Alk24
T23:T24	Alk24:Alk25
T24:T25	Alk26:Alk27
T26:T27	Alk27:Alk28
T27:T28	Alk28:Alk29
T28:T29	Alk30:Alk31
T30:T31	Alk32:Alk33
T32:T33	

Table 5. GC-MS Instrumental Parameters

	Method 1	Method 2	Method 3
Instrument	Agilent 7890A GC/5975C MS	Agilent 7890 GC/5975 MS	Agilent 7890B GC/5977B MS
Column	Agilent J&W HP-1MS 30 m x 0.25 mm x 0.25 µm	Agilent J&W DB-1MS 25 m x 0.20 mm x 0.33 µm	Agilent J&W HP-5MS Ultra Inert 30 m x 0.25 mm x 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 to 1.2 mL/min for 9.97 min 20 mL/min 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	Electron 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 first statistical objective was to determine and quantify significant identifying criteria for medium petroleum products using statistical measures to evaluate the uniqueness and consistency of closely eluting peak pair ratios. The goal was to identify the peak pair ratios that demonstrate the lowest variability across the factors studied. To determine which ratios within the control databases showed the least variability, two-way analysis of variance (ANOVA) was performed, with the two factors being the method location (ML), which refers to the GC-MS method, and evaporation level (EL). For the interpretation of the ANOVA results, a Bonferroni correction was applied and produced a p-value of 0.000424 for the MPDs and 0.001064 for the MIPs. Ratios with p-values greater than the significance threshold are not statistically significantly different and, therefore, show consistency amongst the control samples. The

ANOVA results were organized by a color-coded system to sort which ratios were most indicative of the medium product. The color rankings are described in Table 6.

Table 6. ANOVA Color-Coded Ranking System for Peak Pair Ratios

Color	Rank	Description	NOTES for this Table:
G	Highest	ML and EL ≥ p-value	If all p-values for both variables (ML and EL) were non-significant, meaning consistent ratios, it was ranked the highest and colored Green.
Y	Middle 1	ML only ≥ p-value	If the p-values for ML only were non-significant, meaning consistent ratios, it was ranked the second highest and colored Yellow.
O	Middle 2	EL only ≥ p-value	If the p-values for EL were non-significant, meaning consistent ratios, it was ranked the third highest and colored Orange.
R	Lowest	Both Statistically Significant	If the p-values for ML and EL were both significant, meaning variable ratios across the whole model, it was ranked the lowest and colored Red.

Next, a frequency analysis was performed for the control data and the negative data. This was used to determine the consistency of peaks of interest being present in the control samples but absent in the negative samples. These results were ranked to identify the peaks pairs that are least likely to appear in matrix.

A Wilcoxon Ranked Sum Test was used to compare the patterns of the peak ratios that could be generated in the negative data to the patterns of the peak ratios in the control databases. For the interpretation of the Wilcoxon Ranked Sum Test, a Bonferroni correction was applied and produced a p-value of 0.000595 for the MPDs. This test can only be performed if there are greater than two observations. This was not the case for the MIPs, therefore Wilcoxon results were not used in the subsequent ranking system for the MIPs. The results for the MPDs were ranked by p-value. Ratios with p-values less than the significance threshold are statistically significantly different and are, therefore, more variable between the control and negative samples.

Collectively, these three evaluations were used to create a color-coded ranking system to identify the ratios that met the statistical goals. This ranking system is described in Table 7.

Table 7. Description of Composite Rank Assignments

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

		ANOVA rank is a high number
Red	Lowest Rank	Wilcoxon rank is a high number
		Frequency rank is a high number
		ANOVA rank is a high number

The color-coded ranking system in Table 7 was used to generate the possible point values for the peak ratios, which is shown in Table 8. For the MIPs, no peak ratios were assigned a blue, green, gray, or red rank due to the lack of results for the Wilcoxon Ranked Sum Test.

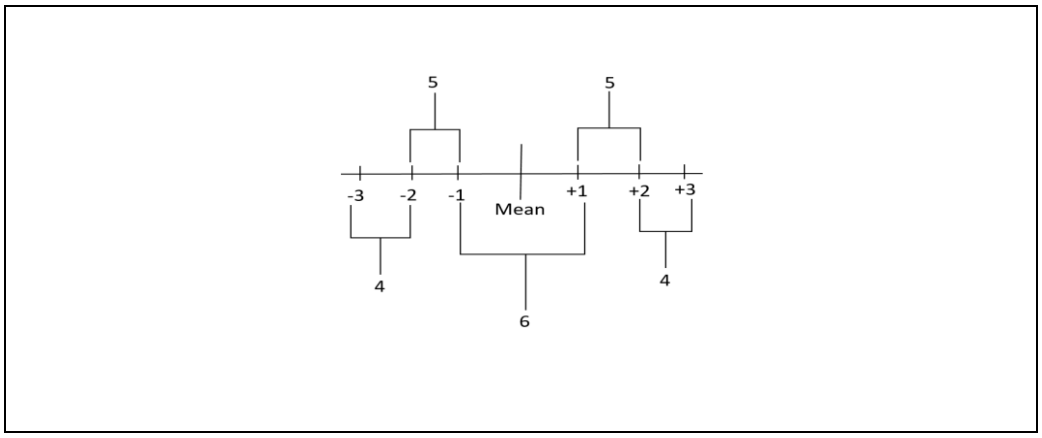
Table 8. Point Values by Rank

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

The peak ratios that make up the red and gray color ranks were excluded from receiving point values for the MPDs because they were not informative or indicative of unique characteristics of MPDs. To generate the point value assignments, a peak ratio that is closer to the sample mean value for that peak ratio from the control database will receive more points and those farther from the mean will receive fewer points. This results in up to three possible point values that can

be earned by each ratio, based on which of three standard deviations the peak ratio falls within (shown in Figure 6).

Figure 6: Point Assignments Based on Standard Deviation



To create the sufficiency curve models the ratios calculated from the control samples were assigned point values based on the standard deviation ranges, as described above. The ratio point values were then summed into two values, a summation of the point values from TIC ratios and a summation of the point values from EIP ratios. The number of TIC and EIP ratios that are in each color-coded rank and the maximum point value for each color rank are shown in Table 9 for the MPDs and Table 10 for the MIPs.

Table 9. MPD Point Values

Color Code	**# of TIC Peak Ratios**	**Maximum Points**	**Total Points per Color Code (TIC)**	**# of EIP Peak Ratios**	**Maximum Points**	**Total Points per Color Code (EIP)**
Purple	8	6	48	12	6	72
Pink	7	5	35	16	5	80
Blue	2	4	8	7	4	28
Yellow	9	3	27	17	3	51

Green	2	2	2	5	2	10
Orange	5	1	5	19	1	19
Total Points			**125**			**260**

Table 10. MIP Point Values

Color Code	**# of TIC Peak Ratios**	**Maximum Points**	**Total Points per Color Code (TIC)**	**# of EIP Peak Ratios**	**Maximum Points**	**Total Points per Color Code (EIP)**
Purple	6	6	36	5	6	30
Pink	6	5	30	7	5	35
Yellow	6	3	18	7	3	21
Orange	6	1	6	4	1	4
Total Points			**90**			**90**

Using the unique, non-overlapping datasets determined by Robust Regression and Outlier Detection (ROUT) method, Linear Discriminant Analysis (LDA) and Quadratic Discriminant analysis (QDA) were performed to generate the decision lines that make up the regions on the sufficiency graph for the MPDs and MIPs. The results were visualized via partition plots. Mixed matrix samples represent samples composed of dilutions of the ignitable liquid under investigation mixed with samples of negative matrix composition in order to mirror the data seen in unknown samples as much as possible. 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 MPD or MIP control data points. This approach removed the samples that would have a visual MPD or MIP 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 an MIP or MPD.

Once the statistical model was completed, the line placement was tested using data sets composed of other classifications of ignitable liquids, GC-MS methods from other forensic laboratories, and reproducibility between analysts.

Highly Evaporated Gasoline Verification

The sufficiency graph for gasoline was created using unevaporated gasoline samples and samples that were evaporated by volume to four levels (25%, 50%, 75%, and 90%). Samples that are evaporated further than 90% were not included in the original study. The existing sufficiency graph workflow was evaluated to determine if it is appropriate for use with more highly evaporated gasoline samples.

Twenty existing and newly purchased gasoline samples were evaporated by volume to the 95% and 99% levels. These samples were analyzed using the three GC-MS methods outlined in Table 5, resulting in 120 gasoline samples. Each was processed using the previously developed gasoline sufficiency workflow.

Summary of Results and Limitations

This study objectively evaluated chromatographic peak pairs present in MPD and MIP samples and used that data to develop statistically supported methods to evaluate an unknown sample for

the presence of an MPD or MIP. The first step in this process was to evaluate known samples to determine the peak pairs that showed the greatest ratio stability, accounting for chromatographic analysis method and evaporation level.

The next step was to evaluate the peak pair ratios from MPDs and MIPs 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 MPDs or MIPs. Figures 7 and 8 graphically display a comparison of the percent presence of each peak pair ratio in the control MPD or MIP database and the negative matrix database. Unlike the previous study on gasoline, none of the peak pair ratios studied for MPDs and MIPs showed a high percent presence in the negative matrix database as compared with the MPD or MIP control databases. Many peak pair ratios were not present in the negative matrix database.

Figure 7: Percent Presence of Each Peak Pair in the MPD and Negative Databases

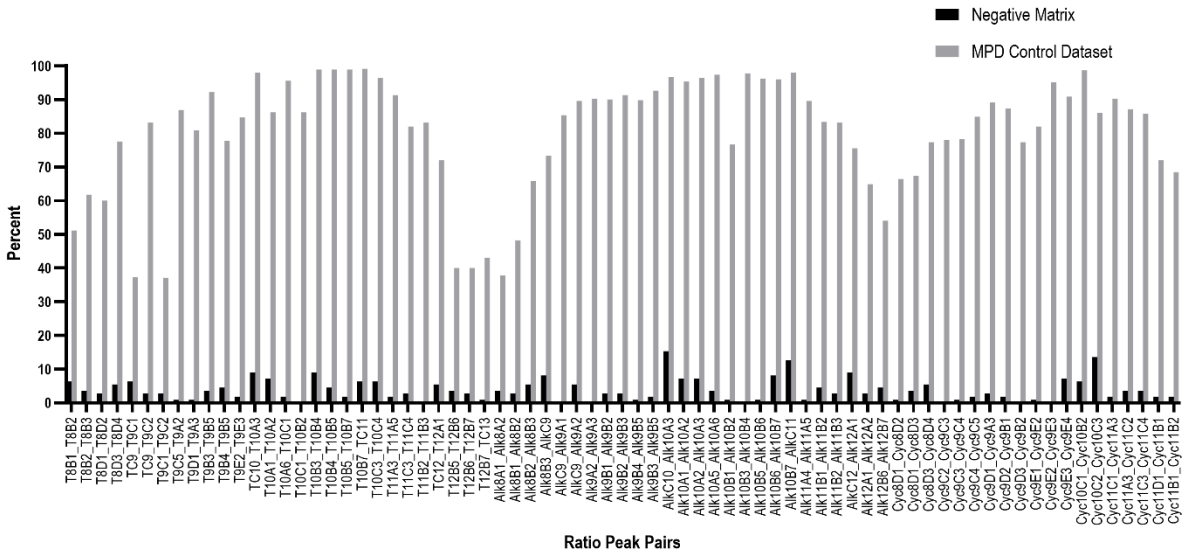


Figure 8: Percent Presence of each Peak Pair in the MIP and Negative Databases

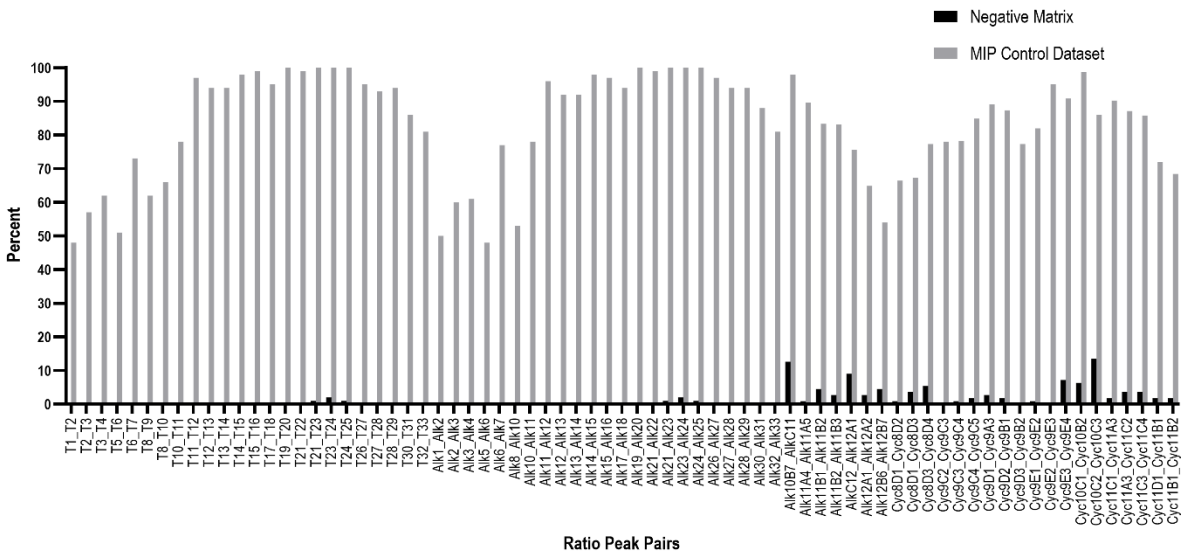


Figure 9 displays all the data points from the evaluation of MPDs. This includes MPD control samples, negative matrix samples, matrix samples mixed with MPD, MPD samples analyzed on additional forensic laboratory methods, other ignitable liquids and a reproducibility study between trained analysts. Figure 10 displays the same type of datasets for the MIP study. The scatter plots show the separation of the MPD and negative samples, and the MIP and negative samples. Unlike the study involving gasoline, a continuum of data (data points extending from the positive control datasets to the negative matrix datasets) from matrix samples with MPD and matrix samples with MIP are not fully established and the majority of these samples overlap with the control samples. This is more pronounced with the MIP dataset.

As published for friction ridge analysis and previously adapted to analysis for gasoline, in a sufficiency graph, the solid curve dividing line defines the lower limit of sufficiency below which an ignitable liquid cannot be identified and further review or analysis is not warranted.

The dotted upper curve indicates the boundary between complex and non-complex samples. In the area between the solid line and dotted line, the data is considered complex and further analysis or review with enhanced documentation is warranted. In the area above the dotted line, the data is considered non-complex and data points have sufficient value to support the identification of the respective class of ignitable liquid.

The approximate expected error rate from the LDA generated decision lines for MPDs was determined to be 0.0081, meaning that the model predicts that approximately 0.81% of future samples would be classified in an incorrect region of the sufficiency graph. The equations for the lines were determined to be $y = -0.62x + 132.59$ for the upper line and $y = -3.46x + 215.61$ for the lower line. These equations were then used to create the sufficiency graph in Figure 9 which includes the data-based decision lines and a heat map to represent the three regions of the graph: red (negative), yellow (complex), and green (non-complex).

The MIP sufficiency graph in Figure 10 demonstrates the overlap of the MIP control and MIP mixed matrix datasets. These are separated from the negative samples. The complex region, or area between the positive and negative samples, is not well represented by the data, rather two regions are present. To capture the polar decisions present, only one decision line is placed using QDA and LDA modeling. The complex yellow region is generated using analysis of perpendicular distance between points above and below the line. The equation for the line was determined to be $y = -1.15x + 71.06$. The approximate expected error rate from the LDA generated decision line for MIPs was determined to be 0.0092, meaning that the model predicts that approximately 0.92% of future samples would be classified in an incorrect region of the sufficiency graph.

For the MPD and MIP sufficiency graphs, any data points falling in the red region, below the lower line, do not have sufficient information for evaluation for a positive result and, therefore, an MPD or MIP 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 an MPD or MIP. The TIC and EIP data for these data points generally show a high level of visual agreement with an MPD or MIP reference sample. These data points are considered non-complex and only require general documentation for the identification. On the MPD sufficiency graph, 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 an MPD. 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. For the MIP sufficiency graph, the complex region is the yellow area near the single decision line. The data points in this region require detailed documentation to support the conclusion.

Figure 9: MPD Sufficiency Graph

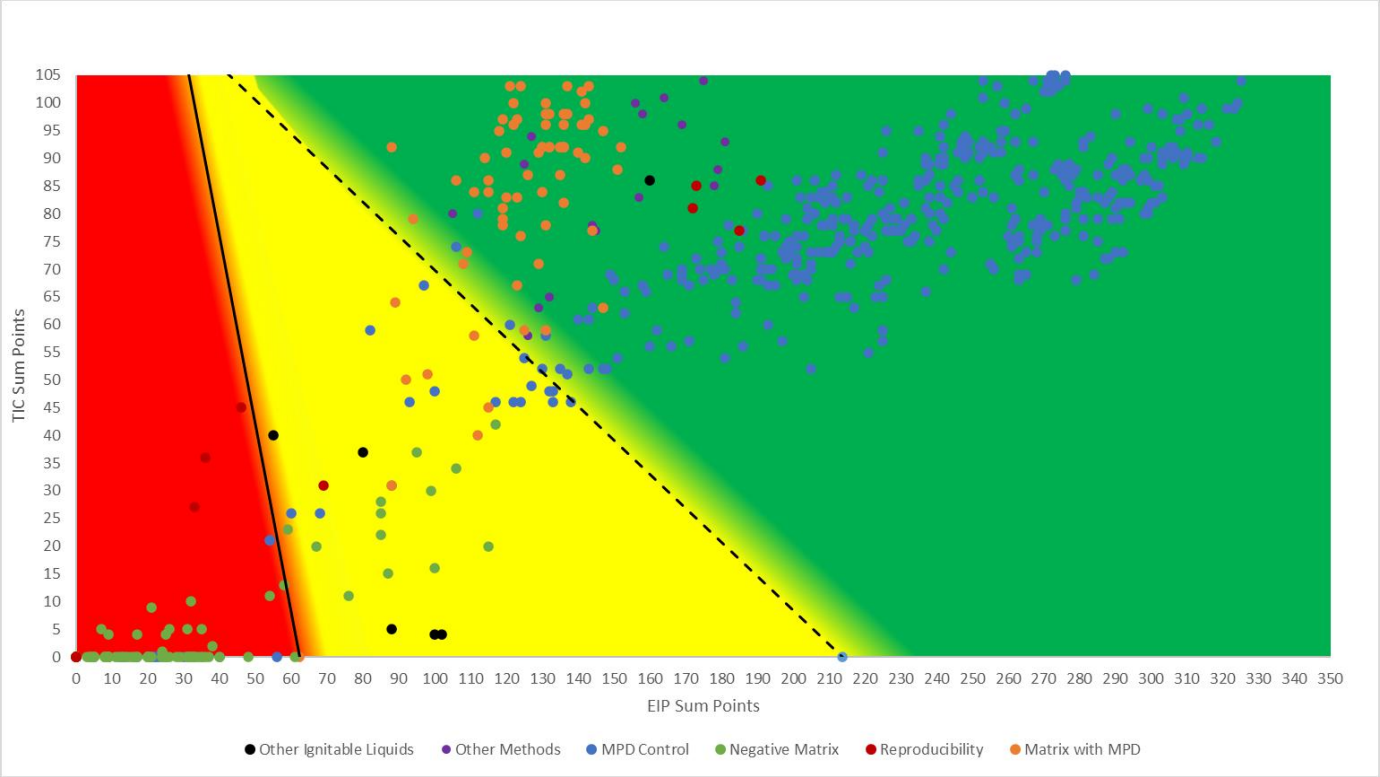
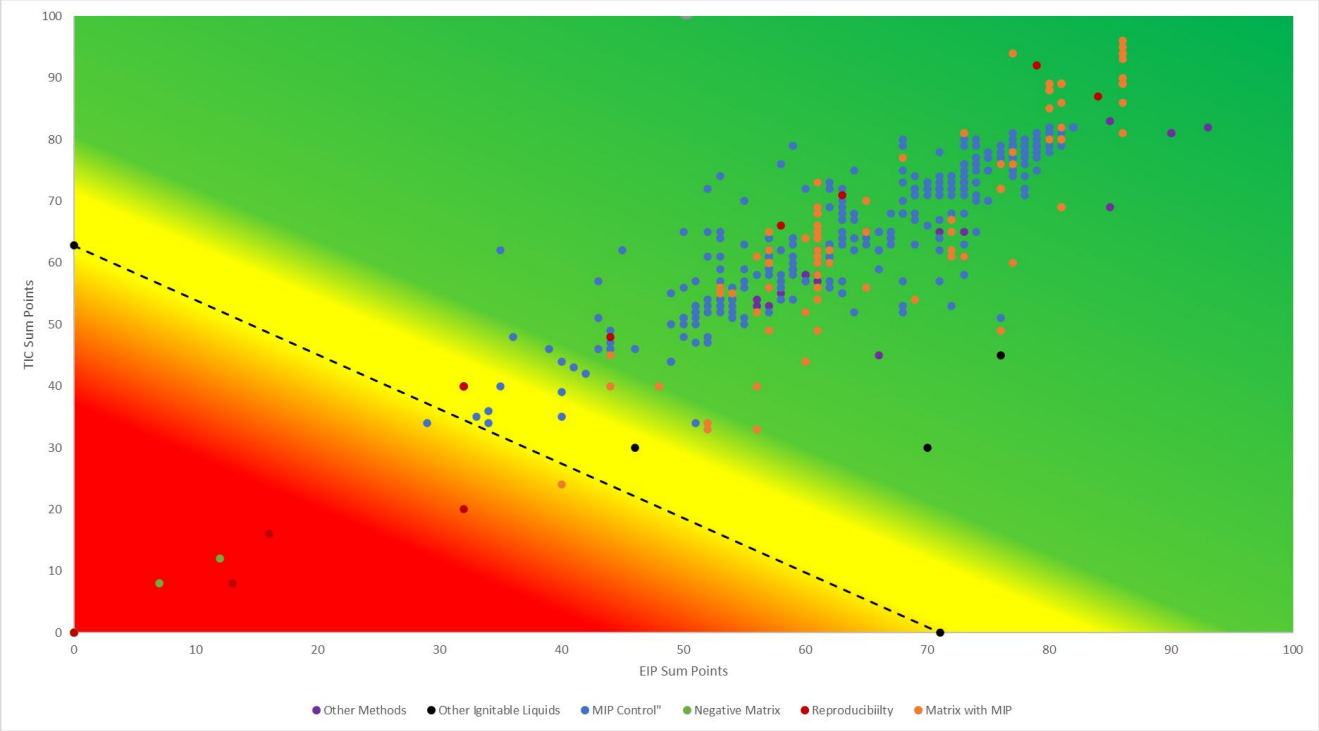


Figure 10: MIP Sufficiency Graph



An evaluation of other ignitable liquid classifications on each of the sufficiency graphs was conducted. Both graphs show potential for misidentification if the sufficiency method was used alone for evaluation of an unknown. The misidentifications are predictable based on the composition of ignitable liquids. A medium naphthenic paraffinic product plotted in the green area of the MPD sufficiency graph while other medium naphthenic-paraffinic products and gasoline samples plotted in the yellow region. Naphthenic-paraffinic products are chemically similar to MPDs but normal alkanes are absent or diminished compared to MPDs. Additionally, petroleum distillates are known to be a portion of gasoline. The ratio between the aromatic and aliphatic contribution of these products must be considered to correctly make the determination. This comparison is outside the sufficiency graph calculations. Gasoline plotted in the green region of the MIP sufficiency graph. Isoparaffinic contribution is a known portion of many gasoline samples. The entirety of the data must be evaluated to determine if gasoline or an

isoparaffinic product should be pursued. Because isoparaffins are a portion of gasoline, a product should not be identified as a mixture of an isoparaffinic product and gasoline.

Figures 9 and 10 each show the results of an evaluation of two known MPD or MIP samples, respectively, analyzed using 10 forensic laboratory GC-MS methods that were not used for the creation of the sufficiency graphs. These consist of five methods using an HP-1 column and five methods using an HP-5 column. All samples analyzed on different GC-MS methods plotted in the green, non-complex region of the graphs.

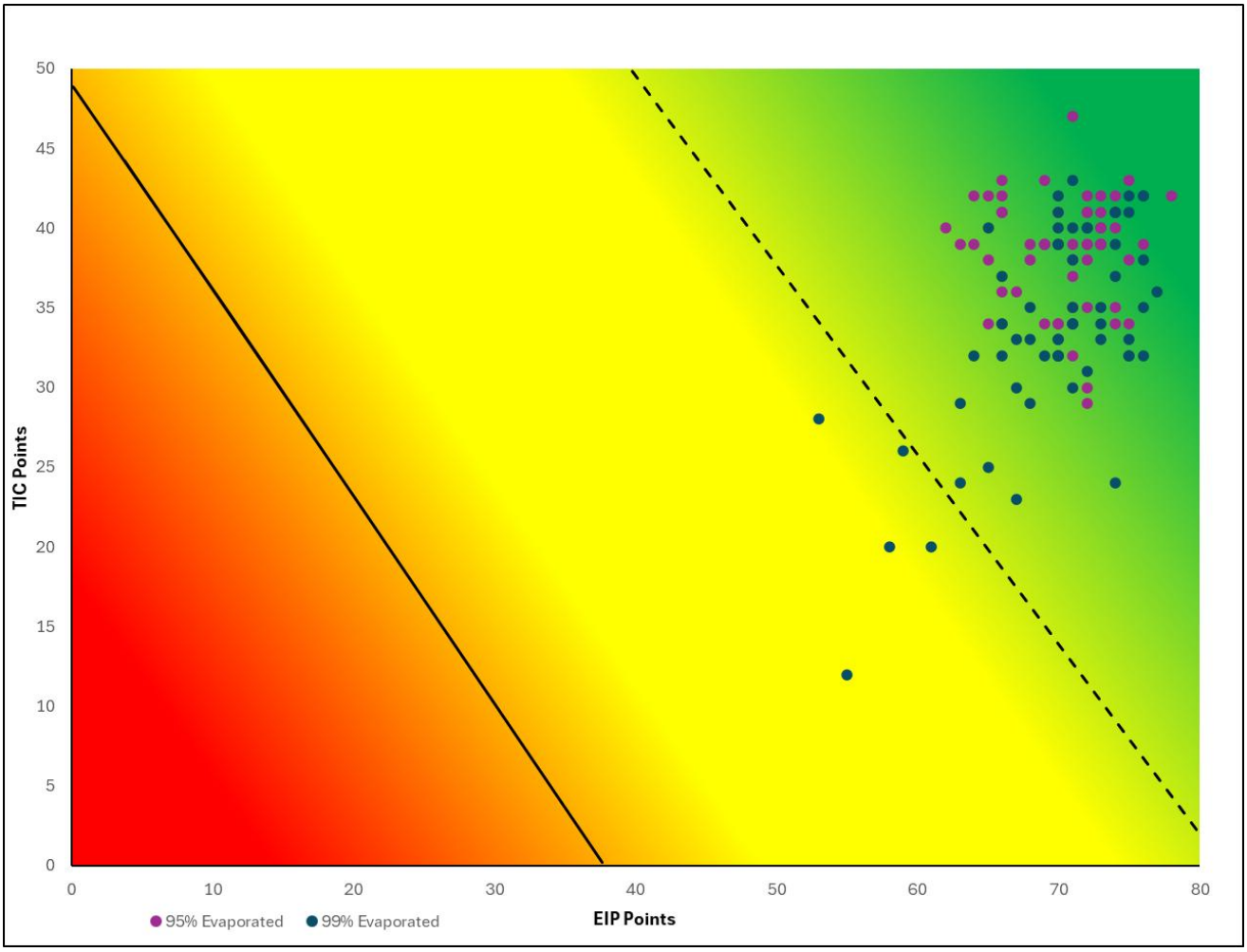
Among the data in the final evaluation depicted in Figures 9 and 10 is a reproducibility study between four trained ignitable liquid examiners at the Virginia Department of Forensic Science. Three samples were analyzed for MPDs and three samples were analyzed for MIPs. The MPD samples show a clustering of data and therefore good reproducibility. The MIP samples do not cluster. Additional training of the examiners may be required to develop more consistency before the sufficiency method for MIPs is implemented.

Highly Evaporated Gasoline Verification

The previously developed sufficiency workflow was determined to be valid for the highly evaporated samples because the samples contained key diagnostic features for gasoline as described in ASTM E1618-19 and the OSAC drafted replacement document for ASTM E1618-19 that has been balloted through ASTM and, therefore, would be subjectively identified as gasoline. Each sample plotted in the green or yellow regions of the graph. The samples that plotted in the yellow region would require transparent documentation if they were analyzed as an unknown sample.

The results of the 95% and 99% evaporated gasoline samples plotted on the previously established sufficiency graph are shown in Figure 11. All the 95% evaporated samples plotted in the green region of the graph showing that they have enough support with this method to be considered non-complex and identified as gasoline. Five of the datapoints for 99% evaporated gasoline plotted in the yellow region, showing that they are complex. For these five samples, the C3 alkylbenzenes are predominantly absent. C3 alkylbenzenes are listed as key diagnostic features for gasoline. The samples from these datapoints would require transparent documentation of the conclusion reached.

Figure 11: Gasoline Sufficiency Graph Depicting Plot Values of 95% and 99% Evaporated Gasolines



Limitations

The previously developed gasoline sufficiency method is robust and very useful, filling a need in ignitable liquid analysis by providing an objective method to determine and display the data present to support an identification of gasoline. The development of the method demonstrated the large overlap in peak pairs between negative matrix and control gasoline samples, further supporting the need for the sufficiency method.

MPDs and MIPs were evaluated to determine if a similar method would be as robust and useful as the developed method for gasoline. The MPD sufficiency method is more difficult to use because of the large number of peak heights collected and the similarity of the chemical composition of most peaks. Petroleum distillates are composed of many branched alkanes which give similar mass spectra and because of the number of isomers, it is virtually impossible to chemically identify the unique isomer present. The isomers do not resolve well, causing the patterns to change depending on the chromatographic analysis method, further complicating locating the correct peak for each peak assignment. Additionally, unlike gasoline, the carbon range of these products is not consistent. Different products have carbon ranges that may or may not overlap, resulting in a wide range of plot values for the green, non-complex region. The most prominent result limiting the utility of the MPD sufficiency graph is the low number of peak pair ratios that were found in common between the control MPD samples and a high percentage of the negative matrix samples. None of the peak pair ratios were found in more than approximately 15% of negative matrix samples, and most peak pair ratios were found in fewer than 5% of negative matrix samples. In contrast, some peak pair ratios from the gasoline study were present in as many as 80-90% of negative matrix samples. This statistically demonstrates that the MPD pattern should not be easily visually confused with a negative sample because the peak pair

ratios should not be present in many negative samples. The MIP sufficiency evaluation showed even less overlap in peak pairs between the MIP control database and the negative matrix samples. The majority of the peak pair ratios were absent from the negative matrix samples. This statistically demonstrates that the MIP pattern should not be visually confused with a negative sample. The MIPs do have more consistency in composition compared to the MPDs, providing more utility of the sufficiency method in that respect. The major limitation in the use of the MIP sufficiency method is the statistically demonstrated lack of overlap with peak pairs from the negative samples.

Applicability to Criminal Justice

The science of fire debris analysis currently lacks standardized, validated interpretation methods for the evaluation of medium petroleum-based ignitable liquids. ASTM E1618-19 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry provides cursory criteria describing the classes of ignitable liquids but does not provide specific criteria for favorable chromatographic pattern comparisons of TICs or EIPs.

ASTM E1618-19 states “the essential requirement for making a classification…is the matching of the sample chromatograms with a reference ignitable liquid chromatogram obtained under similar conditions, noting points of correlation or similarities.” These comparisons can be complicated by the introduction of sample variables such as complex matrix contributions, degradation, ignitable liquid mixtures, or evaporation, which commonly result in complicated patterns from evidentiary samples. Comparisons of complicated sample patterns to known reference ignitable liquids require a high degree of interpretation. Additionally, historical research has focused only on neat ignitable liquid analysis. Currently, conclusions are based on

the training and experience of the examiner and there is no consistent or validated approach used to interpret highly complex samples, which can lead to inconsistent results from one analyst to another.

Although not typically mentioned in the chemistry disciplines of forensic science, subjectivity is in the forefront of discussions regarding physical evidence disciplines such as latent print comparisons, impression comparisons, toolmark examinations and firearms examinations. Within the above context, this study is meant to bolster objectivity in fire debris analysis.

PRODUCTS

Scholarly Products

- *Publications*

  Fire Debris Interpretation Using Quantitative Measures of Chromatographic Features in Medium-Range Ignitable Liquids and the Use of Graphical Display to Demonstrate Data Sufficiency, drafting for Journal of Forensic Chemistrya

- *Databases and Data Repository*

  Data is available on the National Archive of Criminal Justice Data (NACJD). It can be accessed through this link https://deposit.icpsr.umich.edu/deposit/claimResource?tenant=ddf&claimId=172140

Ignitable Liquid Class	**Evaporation**	**Sample Size (N)**	**Instrumental Method**	**Data Points**
Medium Petroleum Distillate Products	Whole, 25%, 50%, 75%, and 90%	30	Two different HP-1 GC columns and one HP-5 GC column	Peak Height (Abundance) and Peak Height Ratios
Medium Isoparaffinic Products	Whole, 25%, 50%, 75%, and 90%	23	Two different HP-1 GC columns and one HP-5 GC column	Peak Height (Abundance) and Peak Height Ratios
Highly Evaporated Gasoline	95% and 99%	20	Two different HP-1 GC columns and one HP-5 GC column	Peak Height (Abundance) and Peak Height Ratios

Dissemination

- *Conferences and Presentations*
    - "Fire Debris Interpretation Using Quantitative Measures of Chromatographic Features in Medium-Range Ignitable Liquids and the Use of Graphical Display to Demonstrate Data Sufficiency," AAFS 77th Annual Meeting, Evening Ignitable Liquid Discussion Group, Baltimore, MD, February 2025
    - "Fire Debris Interpretation Using Quantitative Measures of Chromatographic Features in Medium-Range Ignitable Liquids and the Use of Graphical Display to Demonstrate Data Sufficiency," AAFS 76th Annual Meeting, Denver, CO, February 2024

- *Workshops*
    - Advanced Fire Debris Interpretation, Pinellas County Forensic Laboratory, Largo, FL, October 14-16, 2025
        - The sufficiency method for gasoline was taught at this workshop and the application of sufficiency and results of peak-pair analysis for medium petroleum products were discussed.
    - Is Gasoline Present? - Using a statistically based method to graphically display the support for gasoline in an unknown sample, NEAFS Annual Meeting, Lancaster, PA, October 21, 2025
        - The sufficiency method for gasoline was taught at this workshop and the application of sufficiency and results of peak-pair analysis for medium petroleum products were discussed.

- *Other*
    - Nothing to Report

PRODUCTS

- MPD Data Collection Tool
- MIP Data Collection Tool

Within the Collection Tools (available on NACJD) there are 5 Excel sheets ("Overview", "Peak Map (Printable)", "Peak Names and Ratios", "RT Tracker Sheet (Printable)" and "Getting Started") that have light blue boxes that serve as a description of the tool's elements as well as step-by-step instructions for how to use the tool.

REFERENCES

Christy, B., Winters, K., Rossheim, A., Newman, R., & Tang, L. (2021). 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. *Forensic Chemistry*, *24*, 100337. https://doi.org/10.1016/j.forc.2021.100337

APPENDIX

Validation Summary

To examine the efficacy of the final sufficiency graphs and the placement of the decision lines we followed several validation steps including examining representative samples from other ignitable liquid classes and mixtures of ignitable liquids and examining medium ignitable liquid samples analyzed on GC-MS methods that were not included in the development of the sufficiency graph(s). Additionally, two other analysts were trained and we assessed the overall reproducibility trends of the generated data points. This was done by having the analysts assess the same data files and mapping their subsequent points on the same sufficiency graph. The quantitative standard deviation between the analysts final data points was reviewed, but the qualitative outcome was weighed most heavily.

After testing of the final sufficiency graphs, data collection and analysis tools were created in Microsoft Excel for an analyst to use for the analysis of unknown samples. One tool was created for samples suspected to contain Medium Petroleum Distillates and another was created for samples suspected to contain Medium Isoparaffinic Products. These tools were verified to ensure that they functioned as expected.