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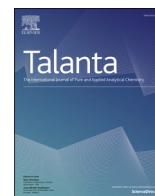
Limits of identification using VUV spectroscopy applied to C8H18 isomers isolated by GC×GC

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ABSTRACT

The vacuum ultraviolet detector for gas chromatography can be used to identify structural differences between isomers with similar chromatographic elution times, which adds detail to characterization, valuable for pre-screening of sustainable aviation fuel candidates. Although this capability has been introduced elsewhere, vacuum ultraviolet spectroscopy for saturated hydrocarbons has been examined minimally, as the similarities between their spectra are much less significant than their aromatic counterparts. The fidelity with which structural differences can be identified has been unclear. In this work, all possible structural isomers of C_8H_{18} are measured and determined to have unambiguously unique vacuum ultraviolet spectra. Using a statistically based residual comparison approach, the concentration limits at which the spectral differences are interpretable are tested in both a controlled study and a real fuel application. The concentration limit at which the spectral differences between C_8H_{18} isomers are unambiguous is below 0.40% by mass and less than 0.20% with human discretion in our experimental configuration.

1. Introduction

Sustainable aviation fuels (SAFs) have been identified as an immediate and long-term pathway to reducing carbon emissions, effective radiative forcing, and the environmental impact caused by aviation [1–6]. Unfortunately, cheap and abundant feedstocks and processes with low capital and operating expenses are clear bottlenecks inhibiting SAF deployment [7]. To resolve these concerns, new SAF candidates are being developed from new feedstocks and processes with the intent of finding multiple methods capable of scaling production up to billions of gallons annually. One method assisting in this development is the introduction of prescreening methods to characterize fuels at low technology readiness levels [7,8]. These early analyses serve as guidance for the refinement of fuel production methods and can offer insight into the likelihood that a production method will pass the qualification, while overall, the capital investment is relatively small.

Analytical chemistry techniques offer value for the early characterization of fuels by providing useful information about the fuel's composition. In general, these methods use volumes on the order of milliliters. This information informs the property models, improving their fidelity, and holds standalone value to fuel producers as it can offer insights on their chemical processes. Compositional information about the feedstocks and the products informs the producers which synthesis pathways are dominating in their process.

A review of property prediction methods has been provided by Vozka et al. highlighting the predictive potential of different analytical methods [9]. In line with the findings of Vozka et al., gas chromatography (GC) techniques are a popular choice for performing this type of analysis. GC methods, especially comprehensive two-dimensional gas chromatography (GC × GC), are highly effective in characterizing fuel composition by both carbon number distribution and hydrocarbon group type e.g. n-alkane, cycloalkane, etc. [10,11]. Historically, this information has been used to identify correlative trends between group types and fuel properties [9,12,13]. With the expansion of large hydrocarbon databases, the need for correlative methods is decreasing as the properties can be calculated directly using first principles [14–17]. The information determined by GC × GC-FID analysis is sufficient to inform several first principles models. However, some properties, such as freezing point and viscosity, are strongly impacted by isomeric structure, which is not informed in standard hydrocarbon group type analysis from GC × GC [9,15,18,19].

The most common detector used with GC × GC systems for fuel

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applications has been the mass spectrometer (MS). MS systems are highly effective at identifying molecular weight and, in turn, molecular formula of a species. Information about molecular formula allows these systems to determine hydrocarbon group type information. However, they have limited capability to distinguish between isomers. From experience with MS, hydrocarbon group type compositional analysis is possible using only GC × GC elution times [20]. The natural progression is to develop methods capable of distinguishing distinct isomers.

Other spectroscopic methods can provide better species-level information than MS. Nuclear magnetic resonance (NMR) can illuminate the connectivity of carbon atoms in single species samples, but this capability diminishes when scaled to complex mixtures. Similarly, infrared (IR) spectroscopy provides information about the molecular structure, which can distinguish some isomeric differences, but also suffers with increased complexity of mixtures. One solution to these issues is to combine advanced spectroscopic techniques with the separation provided by gas chromatography, allowing the analysis to focus on individual structures even on complex mixtures.

In recent years, a vacuum ultraviolet (VUV) detector compatible with gas chromatography systems has been developed. The applications of GC-VUV technologies are still being explored [21–28]. VUV detectors direct ultraviolet light at a sample and the absorbed wavelengths correspond to the energy absorbed by different electronic excitations within the molecule. One strength of the VUV is its identification of olefins, aromatics, and other unsaturated hydrocarbons due to the HOMO-LUMO gaps associated with π-bonds (i.e. double bonds) being centered clearly within the observation region of VUV, around 180 nm. Wang leveraged this strength to utilize VUV as another level of separation to distinguish olefins from cyclo-alkanes, which elute at similar GC × GC retention times and have similar mass spectra [27]. Saturated alkanes, which only observe σ to σ* electronic excitations have less differentiation [29,30]. These differences, although less dramatic, are unique and are the focus of this research.

VUV spectral matching has been successfully performed [21,31–34], but an underlying concern which has not been appropriately addressed until recently [35] is the ability to unambiguously identify matches. Current spectral matching is limited to species within the spectral reference database. If the species being observed are not within the spectral database, it is possible for the species to be falsely identified as a match with another species. As carbon number increases and the number of constitutional isomers follows, the likelihood of misidentification increases. Middle distillates such as jet fuel contain a high fraction of hydrocarbons with carbon number above 10, therefore the concern of misidentifying a species is of particular interest. Previous work has been done to establish methods of identifying differences in spectra [35], but does not fully address the uniqueness of a match.

In this research, all of the constitutional isomers of octane were measured for their VUV spectra and serve as the reference for the following comparisons. It is shown that each of these spectra is distinguishable from one another. For samples of complex mixtures, every chromatographic peak within the elution time boundaries consistent with octanes, is compared against all 18 spectra corresponding to C8 isomers in the freshly built reference library. The spectral library in combination with the spectra matching method of Bell et al. [35] is used to determine the ability of the VUV to accurately and confidently identify structural isomers. Additionally, the concentration threshold at which the measured spectra can no longer confidently determine the structural isomer is determined. This threshold is defined herein as the limit of identification.

2. Material and methods

In this research, the experiments were performed on an Agilent 8890 equipped with a SepSolve INSIGHT flow modulator. The columns are arranged in a reverse configuration with a polar first-dimension column and a non-polar second-dimension column. The first-dimension column is an Rxi-17Sil MS 60 m × 0.32 mm × 0.5 μm from Restek. The second-dimension column is an Rxi-1ms 15 m × 0.32 mm × 0.5 μm, also supplied by Restek. Large internal diameters are used to maximize column loading capacity. Long columns are used to maximize separation at the expense of experimental time. The GC is configured in a dual detector setup with sample going to both a VGA-101 vacuum ultraviolet detector (VUV Analytics) and a flame ionization detector (FID).

Eighteen structural isomers of octane were tested and their spectra were recorded. The species were sourced from various suppliers. A complete list of purities and sourcing is provided in Supplementary Information, Table S1. Each sample was sent through the GC × GC-VUV/FID system (described below). The conventional fuel tested was Jet-A (A-2, POSF 10325) [36]. Additionally, 3-methylheptane and 4-methylheptane were blended with toluene to determine the limits of identification. These blends were made by volume at 0.25%, 0.5%, 1% and 2%. Densities of the blended species were measured and with the volume percentages were used to calculate the mass percentages of 0.2%, 0.4%, 0.8%, and 1.6%, respectively.

Two GC × GC methods were used, one for gathering reference spectra and another for isomer identification. In both methods, the first column flow rate was 1.2 mL/min and the second column flow rate was 48 mL/min with a modulation time of 10 s. The starting temperature for each of the runs was 40 °C where it remains for 30 s and then ramps in temperature at a rate of 1 °C/min. The carrier gas through the GC system was helium (ultra-high purity grade, 5.0) filtered through a Restek Triple filter. For gathering reference spectra, the split ratio was 200:1 with an injection volume of either 0.5 or 1 μL. For the limit of identification blends and Jet A, a method designed for full distillate range fuels was used. In this method, the temperature ramps up to 280 °C, with a split ratio of 100:1 and an injection volume of 5 μL.

The columns were selected to maximize separation in both dimensions and to provide as much sample as possible to the VUV spectrometer. While oversaturation of VUV absorbance spectra is theoretically limiting for analytes in high abundance, for analytes in low abundance identification is limited by signal to noise ratio. In analyzing fuels, like Jet A, with many species each of which are present in low concentration, signal to noise tends to be the driving factor and oversaturation tends to not be a problem.

A VGA-101 vacuum ultraviolet light detector from VUV Analytics was used to obtain VUV absorption spectra. The detector measures the light transmitted through an observation chamber where the analytes flow. Signal is recorded between 115 nm and 430 nm and stored at 76.92 Hz. The transfer line connecting the GC × GC to the VUV detector is maintained at 275 °C with helium as the system gas. The FID is maintained at a temperature of 300 °C. It is supplied with air, hydrogen, and nitrogen at 400 mL/min, 40 mL/min, and 25 mL/min, respectively. In this work, FID results are exclusively used for quantification. Although VUV is quantitative [37], the FID is used for quantification of the species in the Jet fuel sample due to the robustness and simplicity of the FID. The area percentage response from the FID was used as an equivalent to mass percentage in the real fuel due to the similarities of all hydrocarbons response factors [38].

Using the VUV detector to determine the specific structural isomer requires each of the spectra to be unique. It has been claimed that all structural isomers have unique spectra, but the limits of this claim have not been tested [21].

In this work, background signal taken during a time interval with no analytes passing through the chamber was subtracted from the raw data to obtain the spectra used for comparisons. No data filtering or noise cancellation was applied. Spectra recorded for the individual species was acquired by averaging the response across the largest sub-peak from a single modulation which demonstrated no oversaturation within the VUVision software. These values were recorded for all 18 constitutional isomers of octane. Every species was tested and measured 8 times to demonstrate the repeatability. For several pairings, the differences between spectra are subtle and difficult to discern with the naked eye. To

determine the uniqueness of spectra and the limit of identification, numerical techniques are used to compare the residuals to the overall noise of the data following the methods outlined in Bell et al. [35]. These methods involve looking at residual differences between measured spectra and reference spectra. If the measured spectra and reference spectra match, then the residuals should be similar to the profile of the experimental noise of the VUV, alone. The noise at each wavelength is approximately normal, but with standard deviations affected by wavelength. Proportionally adjusting the residuals relative to the expected noise at a given wavelength enables the residuals to be examined as a set, upon which statistical measures can verify its similarity to white noise (a normal distribution). The results are used to determine which spectra meet the criteria to be a match.

For the limit of identification analysis and real fuel application, an internally developed tool for gathering the spectra across multiple modulations of VUV response was used [31]. Utilizing all the modulations maximizes signal to noise and improves the limit of identification. The statistics based residual method is used to highlight the correct match. As the residual statistics between correct match and non-match converge, the limit of identification is found.

This work focuses exclusively on the isomers of C_8H_{18}. Although there are spectra that are more similar than the spectra presented herein, such as the n-alkane series, from an identification perspective, this is not a pragmatic concern due to the ease with which they can be distinguished using elution times [20].

3. Results

3.1. C8H18 isomer spectra uniqueness

The reference spectra of each of the isomers are shown in Fig. 1 which is divided into 4 groupings of structurally similar isomers to improve clarity. Each color includes a line through the mean and a shaded region representing the full range of 8 spectra measurements for the stated isomer. The repeatability bounds of these measurements is less than the line thickness of the mean for the majority of the spectral range. For any combination of two spectra, when plotted together, there is a clear visible gap between the two spectra's repeatability ranges.

The VUV spectra of all saturated hydrocarbons observe a similar general downward trend between 120 nm and 180 nm, corresponding to

single-electron excitations between (sp3) carbon-to-carbon sigma bonding and antibonding orbitals. The VUV detector captures the quantum energy gaps between different electronic energy states. In saturated hydrocarbons, all of the valence electrons are in σ-bonds. Therefore, all electronic excitations must be of the form σ to σ*, which have similar HOMO/LUMO energy gaps. As a result, when overlaid, many of these spectra have high relative coefficients of determination, R^2, which used to be a common metric for defining quality of match [21, 32,33,39]. Despite visible differences in the spectra shown in Fig. 1, of the 153 comparisons between non-similar spectra, 83 showed R^2 values greater than 0.99 proving high R^2 values, when used exclusively, is not persuasive in determining a spectral match.

Even the most similar pair ($R^2 = 0.9994$) of non-matching spectra, 3-methylheptane and 4-methylheptane, are shown to be measurably different as their repeatabilities are significantly smaller than the differences between the two spectra. Because of their similarity, these two species are highlighted as the focus of the limit of identification study below. In Fig. 2, an example from the limit of identification study shows experimental data of a 3-methylheptane peak compared to reference spectra for 3-methylheptane and the most similar non-matching spectra, 4-methylheptane. Fig. 2a shows the two reference spectra and the raw measured data. The differences between the spectra are particularly apparent in Fig. 2b and c, where the residuals of the non-match dramatically diverge from the green shaded region representing the theoretical range caused by experimental noise alone. The agreement between the correct match and the disagreement of the incorrect match are reiterated by the symmetry/asymmetry of the residuals in Fig. 2d and the lack of linearity of the Q-Q plot in Fig. 2e. As demonstrated in Bell et all, correct matches have residuals with approximately a normal distribution, which will correspond to a linear Q-Q plot.

Beyond the visible differences, the residual statistics for all combinations of reference spectra confirm the uniqueness of each spectrum. This suggests that even in the absence of a comprehensive spectral library, a correct match/non-match determination can be made for many isomers in the jet fuel volatility range. This capability is fundamental to the identification of specific isomers by VUV. The ability to determine the difference between two spectra will depend on the quality of the measured spectra, which, for the application of VUV, is limited by concentration and experimental conditions. Below some threshold analyte concentration, the ability to differentiate its spectra from those of
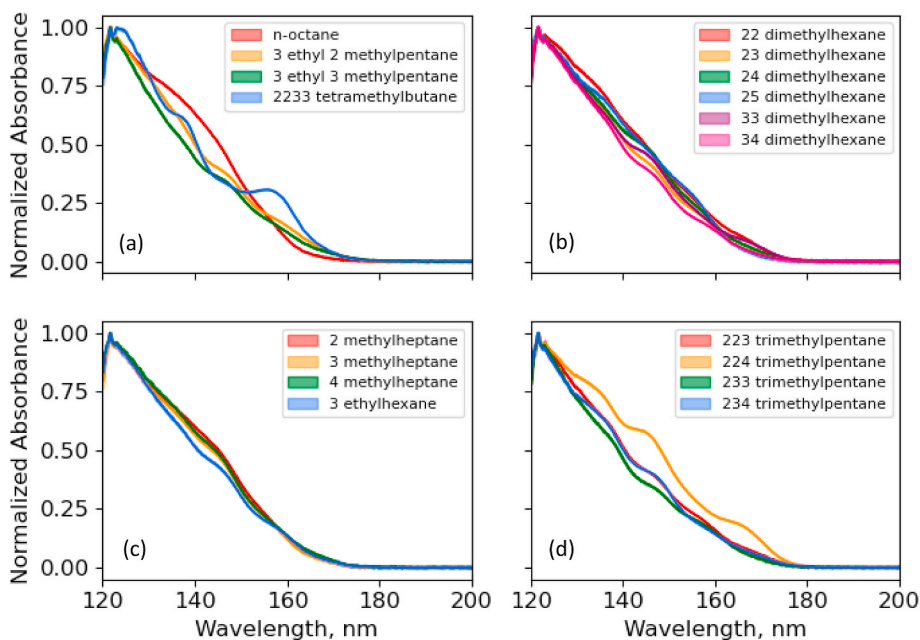

Fig. 1. The spectra of every constitutional isomer of octane is shared. The isomers are grouped into subplots (a–d) by structural similarity for clarity. Each of the spectra is visibly different form the others. The species are grouped with similar species structurally to demonstrate their differences. A solid line is drawn through the mean of the 8 separate unfiltered spectra measurements; The range of 8 separate spectra measurements are the shaded region. The range is less than the thickness of the line in most cases. This demonstrates the spectra are discernably different from each other.
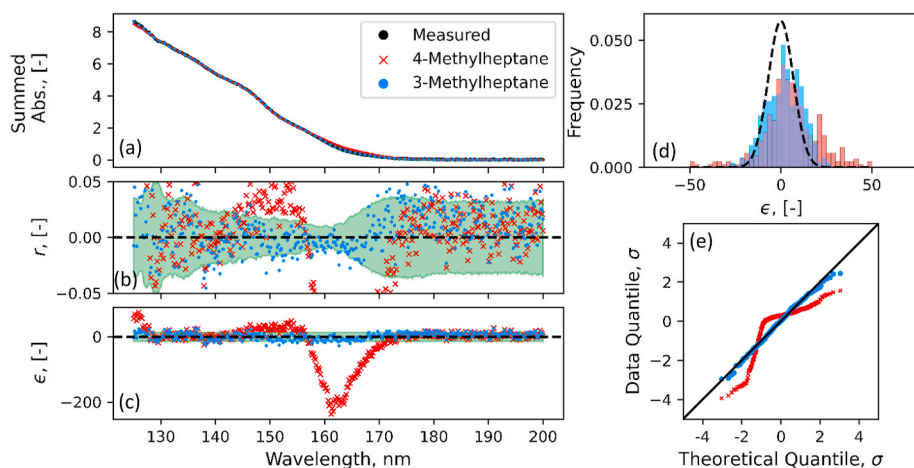
Fig. 2. Comparison of VUV residuals of the 3-methylheptane peak (1.6% mass) in a 3-methylheptane/toluene blend. The correct match and the most similar non-match, 4-methylheptane, are compared to the measured VUV response. This includes the (a) measured VUV signal and reference spectra, (b) standard residuals, (c) residuals normalized based on the noise associated with that particular wavelength, (d) the noise adjusted residual histogram, and (e) the QQ plot testing the normalcy of the residuals.

other species will be lost because the VUV signal will be too low relative to the noise. This concept we call the limit of identification, which is different from limit of detection. The limit of detection is the smallest amount of sample needed for the VUV to detect its presence.

3.2. Limit of identification

Here, 3-methylheptane identification was evaluated against other isomers in increasingly dilute concentrations with toluene. The concentration at which the non-match statistics resemble the statistics of pure noise, as the correct match shows throughout the test sequence, is defined here as the lower limit of identification. The statistical metrics, reported in Fig. 3 with filled symbols, were compared for the correct match and the most similar non-match spectra, which is that of 4-methylheptane. In Fig. 3, the correct match (3-methylheptane reference spectra) statistics are reported with a blue circle. Non-match statistics (reference spectra of other isomers) are reported with an 'x' symbol. The reference isomer with the second highest R^2 value is highlighted with red symbols. The green horizontal bands reported in Fig. 3 report the 95% confidence intervals for theoretical distributions. The derivations

of these distributions are discussed elsewhere [35], and here the distributions are included so the reader can compare theoretically ideal statistics to those of experimental observations. Finally, the open symbol observations (at 0.16%m) are discussed in the following sub-section titled Real Fuel Application.

R^2 values for both matched and non-matched spectra are reported in Fig. 3a. Of particular note, at 0.8%m, the highest R^2 value for a non-match, 0.9943, is greater than it is for the match, 0.9940. This observation, corroborating previous results [35], illustrate that the R^2 as an identification tool is highly limited in the identification of analytes with VUV spectroscopy. The other metrics reported in Fig. 3b–f leverage noise statistics to distinguish a correct match from a non-match. For these statistics, non-matches approach theoretical match statistics in increasingly dilute mixtures. As the noise increases relative to the signal, the contribution of the spectral differences gets overwhelmed by the noise and, correspondingly, the residual statistics converge to the expected results of theoretical noise.

The statistical results at 0.4%m unambiguously suggest the correct, 3-methylheptane identification. All other isomers show statistics unattributable to noise alone. At 0.2%m, the numerical characteristics of the
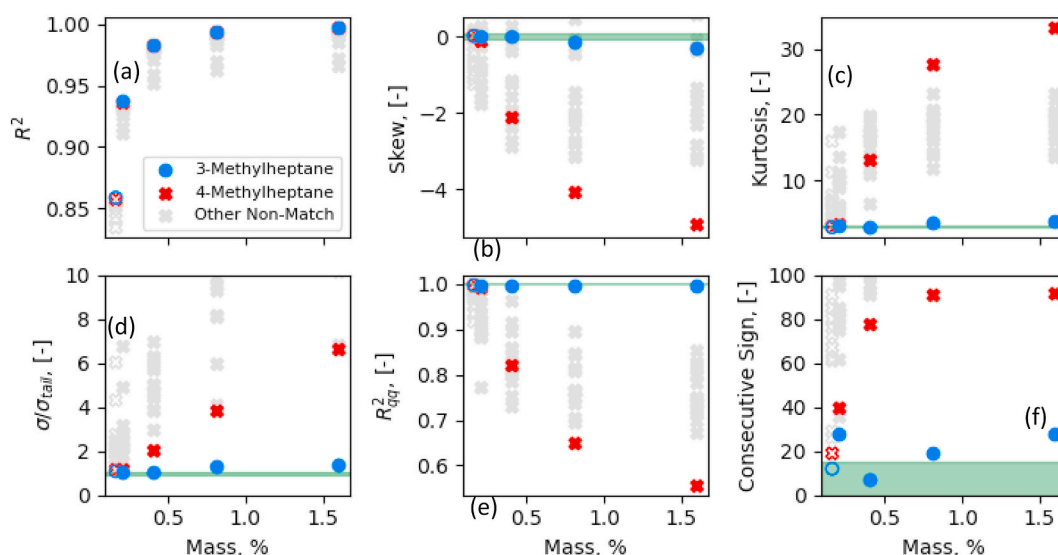

Fig. 3. The statistical results from VUV residuals between multiple reference spectra and measured spectra of a 3-methylheptane peak in 3-methylheptane/toluene blends at various concentrations (solid symbols) and a 3-methylheptane peak in Jet-A (empty symbols). (a) R^2 is shown to be ineffective at discerning matches from non-matches, having non-match results significantly higher than true-match R^2 at lower concentrations. Conversely, (b) skew, (c) kurtosis, (d) standard deviation ratio, (e) R^2_{qq}, and (f) consecutive sign statistics each show true matches having near theoretical (green shaded region) results, while non-matches show convergence to this value with decreasing mass%.

residuals between the analyte and each of the top two matches converge. At that limit, the statistics summarized in Fig. 3 suggest that the reference spectrum for 3-methylheptane is the best overall match to the analyte's spectrum, which is known from experimental design to be 3-methylheptane. However, the next best match, the reference spectrum for 4-methylheptane, (arguably) cannot be ruled out as a potential match to the analyte based solely on this comparative data. Additional information, such as elution time which comes from the same experiment, can bolster the argument for the correct identification, but for the purpose of this discussion such data does not contribute to the identification limit, which is very clearly less than 0.4%m and somewhere close to 0.2%m. Below the identification limit, it is still possible to (dramatically) reduce the magnitude of input uncertainties in predictive properties models [14,40], because many isomers of the hydrocarbon class can still be proven to be non-matches to the analyte and thus ruled out as potential matches. In the conservative case, 16 out of 18 isomers can be excluded at 0.2%m based on statistics alone. With human discretion in observation of the residuals, the conclusion can be narrowed to only the correct match, 3-methylheptane.

3.3. Real fuel application

With a determined limit of identification from the results in Fig. 3, the conclusions are explored for their application in a real fuel sample. A peak from the C8 iso-alkane region was selected from a Jet A sample, A-2 (POSF 10325) [36]. From the quantification performed using FID, the mass percent of this peak was measured to be 0.16%m. The same procedure illustrated above was used to identify this peak. The statistics for this peak are presented in Fig. 3 as open symbols, with the same corresponding color and symbol schema used in the preceding section. The GC × GC chromatogram of the real fuel sample is available in supplementary information, Fig. S1.

The analysis of the residual between the analyte spectrum and the reference spectrum for 3-methylheptane or 4-methylheptane is presented in Fig. 4. Similar to the 0.2% mass example in Fig. 3, the residual statistics in Fig. 5 show that the 3-methylheptane is the best match, but 4-methylheptane arguably should not be ruled out as a match. The results indicate this peak is likely 3-methylheptane, but the conservative conclusion is that it is either 3-methylheptane or 4-methylheptane. At concentrations below the identification limit, the distinction of a match versus non-match become subjective and at the discretion of human interpretation.

With closer observation, the residuals in Fig. 4b and c from 160 to 170 nm strongly suggest that 3-methyl heptane is the correct match.
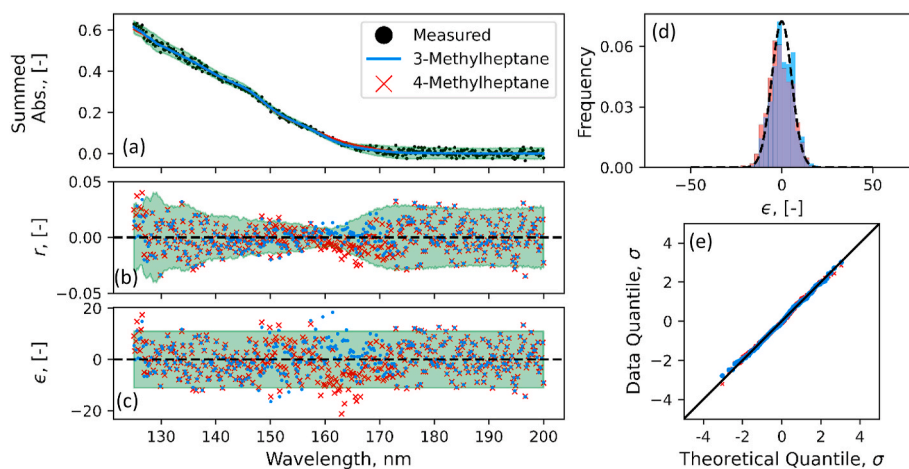
Fig. 5. The residual statistics for the six most likely matches for the C_8H_{18} peak in Jet-A.

Specifically, between 160 nm and 170 nm, there is a clear bias in the residuals of 4-methylheptane to negative values, suggesting 4-methylheptane is unlikely to be the correct match. Regardless of interpretation, the similarities between the results shown in the Jet A sample as compared to the limit of identification study confirm the validity of the statements made about the limit of identification for this application by residual analysis alone.

4. Discussion

Determining a match versus a non-match is fundamentally driven by the limit of identification, which encapsulates the concept of residual analysis and other potential matches. Theoretically, in the case of perfect measured and reference spectra, only the reference spectra are needed to determine a match. No additional isomers or non-match spectra are required. In reality, this is not the case. Data contain noise and are recorded at discrete intervals. As a result, a non-match is more or less defined if a sufficient fraction of residuals (r and ε) lay outside the

Fig. 4. Comparison of VUV residuals of a peak in Jet-A. The two most likely matches, 3-methylheptane and 4-methylheptane, are compared to the measured VUV response. This includes the (a) raw data and reference spectra, (b) standard residuals, (c) residuals normalized based on the noise associated with that particular wavelength, (d) the noise adjusted residual histogram, and (e) the QQ plot testing the normality of the residuals.
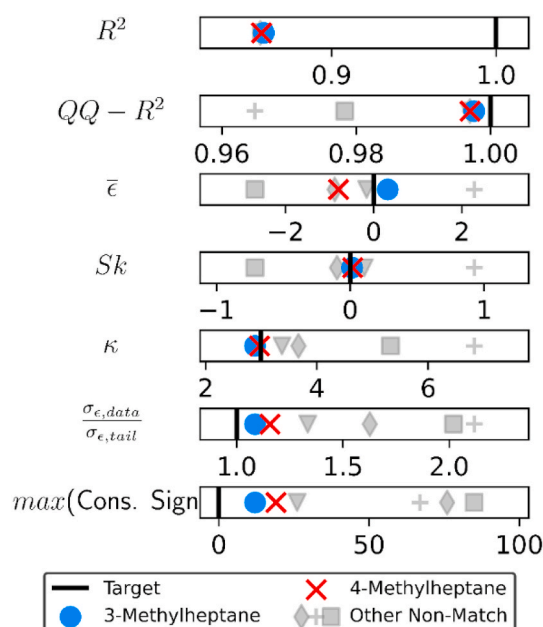
noise distribution (green). The limit of identification is then the concentration at which non-match residuals begin to fall mainly in the noise distribution (green). As illustrated here, this limit is empirical and requires a complete set of potential analytes.

The limit of identification is unknown for regions with an incomplete spectral library, as empirical data are needed to determine the limit of identification. As the molecular weight of an analyte increases, the number of isomers corresponding to that molecular weight increases, and the minimum spectral differences between two different isomers within the set are assumed to decrease. This implies that the limit of identification may increase to higher concentrations for higher carbon number analytes, but it is still possible to rule out most isomers within the set. Instead of identifying an analyte as a distinct isomer, it may be identified as any one of a few (single digit) isomers from a set of hundreds of isomers that have the same molecular weight.

The benefit of the residual analysis approach is the limit placed on false positives. As alluded to above, true positives are limited by (a) the existence of the correct spectra in the database and (b) the identification limit for the analyte of concern. The second issue concerns concentrations or signal-to-noise ratios of the analytes and reference spectra. However, the first issue, with limited datasets, compounds the second issue. Incomplete databases make general assessments of limits of identification difficult. The physical differences between the spectra of two isomers would need to be highly predictable and related to VUV signal-to-noise ratios to only need the correct spectra to accurately identify an isomer with incomplete reference spectra. Hence, absolute conclusions with incomplete databases are limited to confirming true negatives, which provides direct value through the process of elimination and can be applied to methods such as Heyne et al. to reduce uncertainty in property predictions [31,40].

The limit of identification does not suggest that peaks in smaller concentrations provide no value. The spectra can still be used to conclude many non-matches and reduce the number of isomers that a peak could be through the process of elimination. Additionally, the conclusions about the limit of identification apply to the experimental arrangement used in this work. Many factors will impact the limit of identification, including lamp health, column dimensions, injection volume, and species of interest. This work establishes a method for describing these limits in a robust, numerically defensible manner.

A further detail which will restrict the limits of identification is the presence of coeluting species. Some species, even with GC × GC, elute at the same time. When coelution occurs, the required mass of the peak will be appreciably larger. The VUV has a unique ability to deconvolute coeluting species [21,31]. However, the added parameters of determining which species are present and the relative concentrations of each make this analysis significantly more complex.

When exploring conventional fuels, past knowledge and experience provide some amount of knowledge as to what species might be present in a fuel. With alternative fuels, this is not necessarily the case. Although synthesis pathways frequently have expected products based on process-specific decisions, neither the expected products nor the production pathways are required information for fuel characterization with the proposed methods. To accomplish this, thorough spectral libraries are necessary, so expanding these libraries is important for full distillate fuel identification. Ideally this would be accomplished by direct measurement of every species, but this rapidly becomes overwhelming as the number of possible isomers expands dramatically with carbon number (e.g. 60,523 isomers of $C_{18}H_{38}$). The natural progression is to use computational methods to predict spectra, which has been explored, showing predictive fidelity much lower than the required accuracy for spectral matching [29,41]. General trends have been captured, but the details necessary to distinguish isomers still need improvement. Likewise, other properties, such as density, viscosity, etc. are also not available for every isomer of hydrocarbons with high molecular weight.

5. Conclusions

Isomeric level identification is a challenge for hydrocarbon fuel analysis but one that offers huge scientific and practical implications. The VUV detector in combination with a thorough comparison of every relevant pair of spectra are shown to unambiguously identify C_8H_{18} isomers to <0.40% mass, absent a human in the loop. With a human interpreting residual data, this work demonstrates the ability to make correct identifications to ~0.20% mass. The work shows the tremendous repeatability of the measurements, which enables the confident identification of visibly small differences between two spectra. The combination of GC × GC with a VUV detector enables improved separations as compared to traditional GC-VUV arrangements but also allows for carbon number information to be known before VUV spectral matching attempts. The complementary nature of chromatographic elution times with the structural information provided by the VUV makes for a powerful tool for chemometrics.

Credit author statement

David C. Bell: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – Original Draft. **John Feldhausen**: Conceptualization, Data Curation, Formal Analysis, Methodology, Software, Validation, Visualization, Writing – Review & Editing. **Aaron J. Spieles**: Investigation, Methodology, Validation, Writing – Review and Editing. **Randall C. Boehm**: Supervision, Writing – Review and Editing. **Joshua S. Heyne**: Conceptualization, Funding Acquisition, Supervision, Writing – Review and 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2023.124451.

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