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Gas chromatography—vacuum ultraviolet spectroscopy in petroleum and fuel analysis

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Abstract

In the modern world, energy and fuels are of utmost importance. Rapid characterization of petroleum and other hydrocarbon-based fuel is a well-researched field. Gas chromatography has traditionally been used to separate the different species and characterize the chemical content in fuels. Ideally, every molecule would be separated and characterized, but due to the complexity of the petroleum matrix, many compounds coelute. With the help of different detectors, more information can be gained, but there does not exist a single detector that can unambiguously differentiate and identify every compound. Vacuum ultraviolet spectroscopy (VUV) is a relatively new detector that can alleviate many limitations of other detectors. Based on spectroscopic absorption, VUV detection can provide qualitative and quantitative information regarding the composition of different fuels. It also provides certain advantages, allowing the deconvolution of coeluting peaks and differentiation between constitutional isomers. VUV has been used to classify the range of chemical components in many diverse fuel samples. Here, the contributions of VUV detection to petrochemical analysis to date are reviewed.

KEYWORDS

ASTM, fuels classification, gas phase absorption, PIONA, pyrolysis oils

1 | INTRODUCTION

The association between petroleum and human civilizations has existed since a black substance called 'mum' bubbled out of the dead sea. This dead sea asphalt was so precious that it was exported to be used in the funerals of kings to perform mummification.¹ Petroleum and its products were one of the major driving forces of technological development in the 19th and 20th centuries.² The world relies on these chemicals, as evidenced by the over \$500 billion petrochemi-

cal market worldwide.³ Due to the importance of petroleum fuels and their feedstocks, determination of the composition of petroleum and its derived products in an efficient and inexpensive manner is of utmost importance.

The composition of petroleum is complicated; many thousands of individual compounds are found in petroleum, and each varies in size, structure, functionality, and polarity.⁴ Their complexity can be demonstrated by examining the number of alkane isomers that can form at each carbon number and how this number increases with carbon number. When there are five carbons, there can be three isomers; eight carbons can be arranged into eighteen isomers; fifteen carbons yield 4347 isomers; and alkanes that contain twenty carbons total 3.66×10^5 isomers. One can expect alkanes of twenty carbons or even higher in certain petroleum products, such as heavy fuel and

Abbreviations: DHA, detailed hydrocarbon analysis; FID, flame ionization detector; GC, gas chromatography; GC×GC, comprehensive two-dimensional gas chromatography; HRMS, high-resolution mass spectrometry; MS, mass spectrometry; PIONA, paraffin isoparaffin olefin naphthene aromatic; TID, time interval deconvolution; VUV, vacuum ultraviolet spectroscopy.

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TABLE 1 A table showing the different distillation products of petroleum, with their carbon number and boiling point range shown. It is of note that the cutoffs can vary slightly depending on interpretation.⁶⁹

Petroleum product	Carbon number	Temperature range °C
Gases (propane, butane)	1–4	0–30
Naphthas (gasolines)	5–10	30–180
Kerosenes (jet fuel)	10–16	180–260
Gas oils (diesel oil)	16–60	260–350
Lubricants	60+	350–575
Fuel oils (ships, factories)	70+	490+
Asphalts	80+	580+

lubricating oils. Besides alkanes, there are a variety of other compound classes present.

Due to the many different molecules found in crude oil, standard classifications have been created to assist in discussing petroleum composition. The non-heteroatom-containing hydrocarbons can generally be classified as paraffins (P; linear alkanes), isoparaffins (I; branched acyclic alkanes), olefins (O; alkenes), naphthenes (N; cyclic alkanes) or aromatics (A; containing at least one aromatic ring). These simplified categories are the primary way to describe different fuels, commonly referred to as PIONA analysis. Petroleum can also contain molecules with different heteroatoms, including sulfur, nitrogen, oxygen and metals. Reviews discussing methods for understanding the heteroatom-containing molecules in petroleum have been communicated, as each heteroatom can have a different effect on the fuel and its processing.^{5–7}

Since its invention, gas chromatography (GC) has been used to examine petroleum and its refinery products and has remained a primary technique for hydrocarbon fuel analysis.⁸ GC can analyze compounds with a boiling point range up to and above 400°C. Table 1 shows the different distillation fractions of petroleum with their carbon number and boiling point range. These carbon numbers and boiling point ranges can vary slightly based on interpretation. While GC itself can provide pertinent information about petroleum products, it is limited in its separation power. More modern GC analysis has used multi-dimensional techniques such as comprehensive two-dimensional gas chromatography (GC×GC), which can provide group-type analysis of petroleum and its products.⁹

While GC has been the separation technique that has dominated the petroleum industry, different detectors have been used, as each has its own advantages and disadvantages. The flame ionization detector (FID) has had a significant and consistent role due to its selectivity for compounds containing carbon bonds and its reliability for accurate quantitative data. The primary disadvantage is that the FID does not provide any qualitative information.¹⁰ Mass spectrometry (MS) is another standard detector in fuel analysis, as it is a nearly universal detector that provides structural information and quantitative data. Specifically, high-resolution mass spectrometry (HRMS) has been utilized in petroleomics, the complete characterization of petroleum

down to the molecular level.^{11–14} Depending on the ionization source, almost every molecule can be identified as the mass analyzer can differentiate molecules down to 0.001 Da. The downside of mass spectrometry is that it cannot easily differentiate between constitutional isomers, enantiomers, and many isobaric compounds; high-resolution mass spectrometers are also costly. Other detectors commonly used in petroleum analysis, such as nitrogen-phosphorus detectors and sulfur chemiluminescence detectors, do not have broad applicability as they only detect specific compounds. However, they are conducive to analyzing specific classes, such as sulfur-bearing hydrocarbons. A variety of other detectors could be considered for certain applications.¹⁵ Electron capture detection and negative chemical ionization–MS are particularly sensitive to halogenated and electronegative compounds.

A detection technology that is being adopted in the petroleum industry is the vacuum ultraviolet absorption spectroscopic detector (VUV) for GC (GC-VUV). This work will review why the VUV detector has improved the examination of different hydrocarbons, primarily due to its ability to solve many of the issues associated with traditional detectors. The VUV detector can facilitate rapid analysis through the ability to deconvolute coeluting peaks, supply class-specific absorption spectra with predictable response factors for library searching and qualitative analysis, differentiate hydrocarbon isomers, and provide quantitative information. Two previous reviews have discussed the development and use of GC-VUV, one in 2017 and another in 2020.^{16,17} Another article discussed the early use of GC-VUV for petrochemical analysis.¹⁸ This work aims not to repeat and update the previous efforts but to focus on the critical application of GC-VUV technology in analyzing conventional and alternative fuels.

2 | VUV

Vacuum ultraviolet spectroscopy is a near-universal detection technique for GC instrumentation.^{18,19} While others have demonstrated the use of ultraviolet absorption detection for GC, there were issues, from high detection limits to limited light sources and wavelength ranges.^{20–23} A new commercial instrument introduced in 2014 (the VGA-100 from VUV Analytics, Inc., a schematic for which is shown in Figure 1) has renewed interest in VUV/UV absorption spectroscopy as a GC detection method; yet, this also shows the relatively young lifespan of this technique, not even a decade old.

VUV detection focuses on the absorption of light in the vacuum ultraviolet/ultraviolet spectral range of 120–240 nm. Previous analytical work in the vacuum ultraviolet range of 115–185 nm required bright source synchrotron facilities and evacuated measurement chambers; the practical application was limited.²⁴ Electromagnetic radiation in the VUV wavelength range can facilitate $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $\pi \rightarrow \pi^*$ transitions for most molecular species. As atmospheric oxygen absorbs these wavelengths strongly, an evacuated environment was traditionally needed to detect compounds using these wavelengths. Fortunately, compounds with minimal absorption characteristics in this region are the common carrier gases used in most GC applications. Hydrogen, helium, nitrogen, and argon all exhibit very weak absorption,

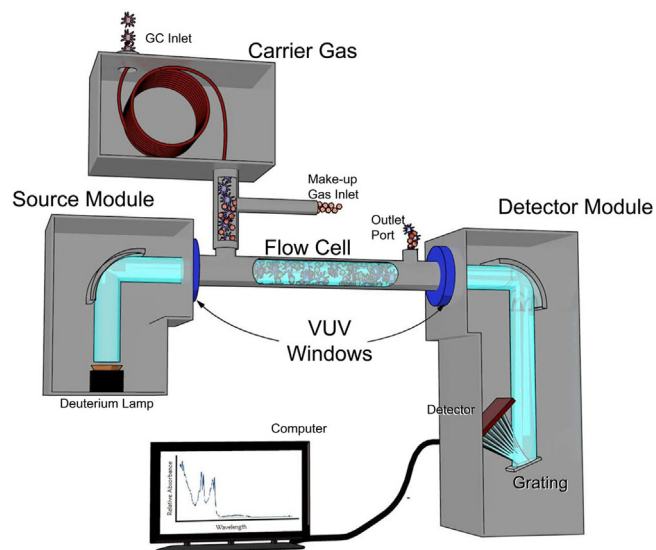


FIGURE 1 A schematic of the VGA-100 (not to scale). The flow cell volume is 80 μL , and the path length is 10 cm. It is important to note that there is no vacuum pump, as one is not needed.¹⁹

and their contribution to spectra can be easily background subtracted. The coupling of modern GC to VUV detection is ideal, and no vacuum systems are present in the detector.¹⁶

The most significant aspect of VUV spectroscopy is that each compound produces unique absorption spectra. Combined with the fact that VUV is a mass-sensitive detection method (where the amount of the analyte is proportional to the detector's response), software has been created to differentiate constitutional isomers, deconvolute coeluting peaks, and perform quantitation. Therefore, VUV is a complementary detector to more traditional detectors, like mass spectrometry, which are limited in differentiating coeluting peaks, as well as distinguishing isomeric and isobaric compounds. Mass spectrometers can deconvolute coeluting signals, but more sophisticated algorithms are needed to accomplish the task, compared to VUV/UV spectroscopy, where measured absorption of multiple species is simply additive.^{25,26} Mass spectrometry can also provide some isobaric differentiation using tandem mass spectrometry, tagging, or ion mobility, but additional capabilities such as these add significant costs.^{27,28} VUV detection provides a complementary lens for compound identification and differentiation, since absorption spectral shapes vary with atom connectivity and bonding within molecules.

The differentiation of xylene isomers is a simple example demonstrating the benefit of VUV detection.²⁹ The isomers of xylene require special columns to resolve chromatographically, and they have identical mass spectra, which inhibits their complete differentiation using GC with other detection techniques. In contrast, the VUV absorption spectra for each of the isomers are different. The different spectra allow facile deconvolution of the overlapping signals, and the contribution of each compound to the observed signal can be easily determined. The most straightforward deconvolution techniques, which rely on the additivity of absorption spectra weighted by the relative abundance of each compound, require that spectra for each of the overlapping

compounds be present in the reference library. However, other more advanced library searching and deconvolution algorithms have also been explored in an attempt to alleviate this limitation.³⁰

Another benefit of the VUV detector is its ability to quantitate using traditional means, such as through internal and external standard calibration, but also to quantitate in a calibration-less fashion through pseudo-absolute quantification.³¹ These quantification capabilities are due to basic Beer-Lambert Law concepts. Pseudo-absolute quantification refers to the ability to quantify different compounds by referencing known absolute absorption magnitudes for an analyte of interest across the 120–240 nm spectral range. As each absorbance spectra is inherent to each molecule, the cross-section, or probability of a molecule to absorb a wavelength, can be used to quantitate the amount of analyte present in the flow cell. This pseudo-absolute quantification can also provide performance checks on the system and solve quantification problems with complex samples. Relative response factors (RRFs) can be used for the classification and relative quantitation of certain species due to predictable changes in absorption intensities among homologous series and related structural features, such as aromaticity.³²

These features have allowed VUV to be applied for analysis in a multitude of applications, including for pesticides, beverages, fatty acid methyl ethers, biological samples, and forensics analysis, among others.^{29,33–37} This has included conventional fuels, oils, and alternatives like plastic waste pyrolysis oils.³⁸ VUV has been shown to provide easier and faster fuel separations than conventional means due to its deconvolution and chemical compound class differentiation properties. Paraffin, isoparaffin, olefin, naphthene, and aromatic (PIONA) content analysis is crucial when comparing different fuels. VUV has shown to be viable for PIONA determination, and VUV detection has been featured in two standardized methods, ASTM D8071 for the PIONA analysis of gasoline and ASTM D8267 for jet fuel.^{39,40}

A downside to VUV is its relatively modest limit of detection and its limited library size. These can and have been improved by technological advancements in subsequent generations of VUV detectors, coupling VUV together with other detection methods, increasing temperature and spectral ranges, and continual augmentation of the VUV spectral library. Efforts have also been made to use computational predictions of VUV spectra for matching spectra to compounds when their library spectra may not be available.^{30,41–45}

3 | TECHNIQUES ASSISTING FUEL ANALYSIS

3.1 | Time interval deconvolution

Time interval deconvolution (TID) has been a beneficial addition to PIONA analysis.^{32,46} Time interval deconvolution uses retention indices, the VUV spectral library, and the Beer-Lambert law to sort the coeluting peaks into respective PIONA categories. The general workflow involves the determination of retention indices before analysis. These retention indices can either be obtained via a homologous series of n-alkanes or through the sample itself using ~10 well-known peaks.

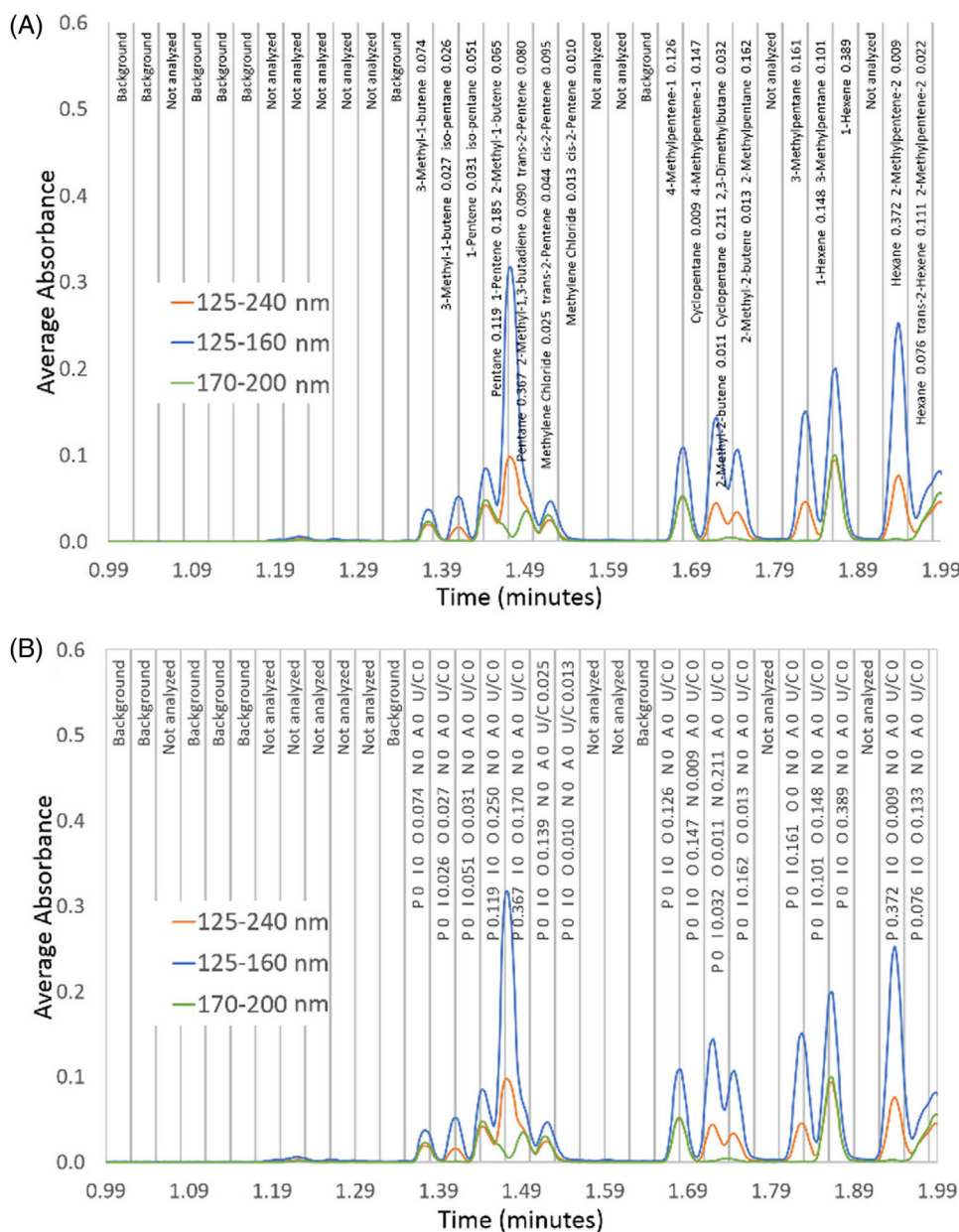


FIGURE 2 An example gas chromatography (GC)-vacuum ultraviolet spectroscopy (VUV) chromatogram of a PIONA standard showing the results of a time interval deconvolution (TID) process. (A) shows the individual species that make up the chromatogram, while (B) shows the PIONA class in each interval.³²

Then a time interval is selected, and a series of steps is performed before proceeding to the next time interval in the chromatogram. The steps involve the calculation of the total absorbance in the time interval, the calculation of the average retention index, a search of the library for compounds with a retention index that matches the time interval, and then determining the proportion of area response for each analyte class present. Once every time slice is analyzed, the program then calculates the mass% of each specified class using RRFs. One does not need to know the individual RRF for each compound, as compounds greater than five carbons demonstrate predictable RRFs for each functional group. TID allows for automatic PIONA characterization quickly, while traditional methods require individual examination

of every peak, a lengthy process. An example can be seen in Figure 2, where different time intervals can be shown, providing both compound identification and PIONA classification.

Gasoline was initially chosen to demonstrate the capabilities of GC-VUV and its use in combination with TID.³² Comparisons were made to ASTM D6730 in this proof of concept. Most of the ASTM methods examined at the time used flame ionization detection (FID), which required precise control of the separation, and even multiple off-line separations performed in tandem to obtain classifications of the group types. This introductory study looked at GC-VUV for PIONA analysis and for detecting different oxygenates. The time interval deconvolution procedure assisted the analysis and found that the GC-VUV data

agreed with that from the ASTM methods. While the TID method was demonstrated for gasoline, in theory, it could be used on any fuel type and in many other compound classification applications. In fact, it should be more beneficial for middle distillates, as their composition is more complicated due to the larger number of carbons present. In principle, this TID method can also be used for characterizing heteroatom-containing species and compound classification in a variety of sample types.⁴⁷

3.2 | GC-VUV and multidimensional chromatography

As multidimensional gas chromatography becomes more of a player in the petroleum analysis field, fast selective detectors will have greater importance. Data acquisition for the VUV detector can be set as high as 100 Hz. Because full wavelength absorption data is collected simultaneously using a charge-coupled device detector, the VUV does not suffer from the need to scan across different wavelengths over time. In this respect, VUV detection is well compatible with comprehensive on-line two-dimensional gas chromatography (GC×GC).

Two similar studies examined diesel fuel and fatty acid methyl ester (FAME) mixtures using GC×GC with VUV detection.^{48,49} Gröger et al. examined a diesel sample with a defined FAME mixture added into its composition.⁴⁸ The original diesel had paraffins, isoparaffins, aromatics and alkylation products, while the unsaturated and esterified compounds originated from the FAME mixture introduced into the sample. They resolved the different components satisfactorily and demonstrated the value of the different absorption spectra for identifying compounds and classes across the GC×GC chromatogram. Zoccali et al. used GC×GC-VUV to analyze a biodiesel sample with a defined FAME mixture as part of its composition.⁴⁹ Results showed how pseudo-absolute quantitation could rapidly determine the relative content of FAME components in the mixture. VUV detection was ultimately shown to be highly orthogonal to the GC separation and provided valuable absorption spectra to aid compound identification when it was combined with the high-efficiency compound class separation achievable using GC×GC.

Lelevic et al. examined middle distillates using a VUV detector hyphenated to multidimensional gas chromatography.⁵⁰ Some current methods that rely on mass spectrometry, for example, ASTM D2425, have been restricted to samples with a limited boiling point range and olefin content. These methods have difficulty differentiating between isomers, and the quantitation is time intensive. Quantitative and qualitative analysis was performed on fourteen different diesel samples from different origins. Results were compared with current methods (including GC×GC-FID with prefractionation, MS and UV spectroscopic analysis) to analyze aromatics and the bromine number for the olefins. Results from GC×GC-VUV agreed well with those from other methods; the VUV-based analysis was faster and provided more information for species classification.

GC×GC-VUV/FID, as a combined detection technique for multidimensional GC, was demonstrated to be a powerful tool for differ-

entiation between different gas oils.⁵¹ When using GC×GC for gas oils, many compound groups tend to coelute; olefins and diolefins tend to coelute with naphthenes, while polycyclic naphthenes tend to coelute with monoaromatics. FID can provide excellent quantitative data but cannot provide any qualitative information. VUV can provide both quantitative and qualitative information, making it attractive in replacing or complementing FID detection in petrochemical analysis using GC×GC. Different compound classes and those with variable carbon numbers have different molar absorptivities. Therefore, RRFs had to be determined and used for quantification of different hydrocarbons. VUV RRFs were created for about 160 different hydrocarbons appearing in gas oils, selected according to their carbon number and group type. The availability of RRFs allowed for direct quantitation of individual components. Fourteen different gas oils of different origins were compared. Analysis using the FID detector required prefractionation, while analysis using the VUV detector did not. Overall, there was good agreement between the two methods. Avoiding prefractionation when using VUV detection can significantly improve the efficiency of analysis, making the detector more attractive.

A demonstration of GC×GC×VUV as a three-dimensional technique was presented to examine a diesel sample by Wang.⁵² Diesel was specifically chosen because it could demonstrate that some isomers chromatographically coelute, and these isomers cannot be differentiated by mass spectrometry or other analytical techniques. The VUV detector was treated as a separation device, using spectral filters to isolate different compounds. An example of this is shown in Figure 3, where olefins were chosen to be the compounds of interest. With the application of an appropriate spectral filter, olefins could be distinctly highlighted relative to the higher abundance saturates.

3.3 | Software and technology improvements

Software and technology improvements are required to evolve methodology. Software development was required to allow VUV to behave as a separation technique. The software to convert GC-VUV analysis into GC×VUV analysis was developed in-house by Wang and involved data rearrangement and a change in data visualization.⁵³ GC-VUV analysis looks at the total absorbance throughout the GC run with respect to time, while GC×VUV analysis provides a full spectrum view for every data point throughout the analysis. The main advantage of viewing the VUV data as a multidimensional separation was to visualize the entire data set and allow visual separation of saturated from unsaturated components. The 3D visualization also highlighted previously unknown group specific absorption bands, which could be used to further assist in group-type analysis, shown in Figure 4. Alkylated triaromatics are characterized by absorption in the 220–260-nm range. When using a 3D visualization, their contributions become apparent compared to a 2D visualization of the same wavelengths. This data visualization method can be used to identify different classes of compounds quickly. This way of viewing information was also compared to GC-FID and GC×GC-FID, and the results obtained were congruent with those obtained using other detectors.

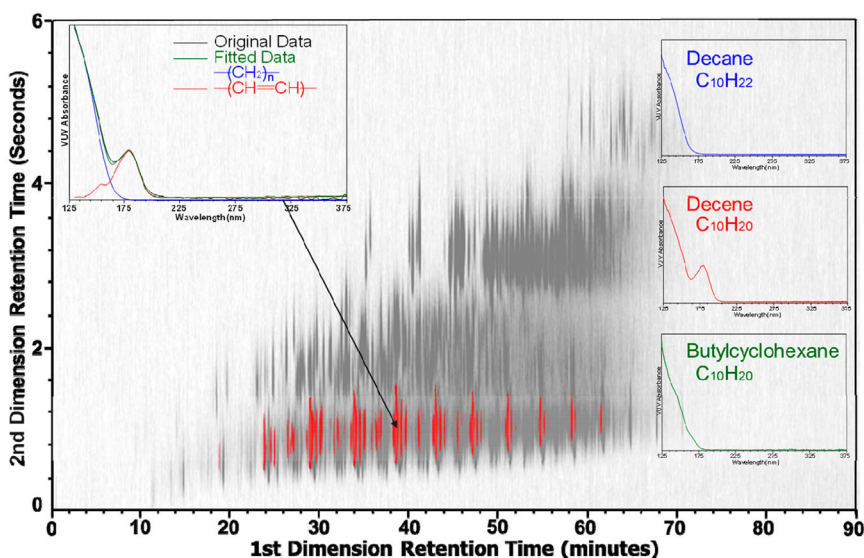


FIGURE 3 An example of a gas chromatography (GC)×GC× vacuum ultraviolet spectroscopy (VUV) chromatogram using diesel as an example sample. The highlighted red region shows olefins. In the deconvolution procedure, the absorption spectra on the side show the seed or example spectra used to find paraffins, olefins, and one-ring naphthenes.⁵²

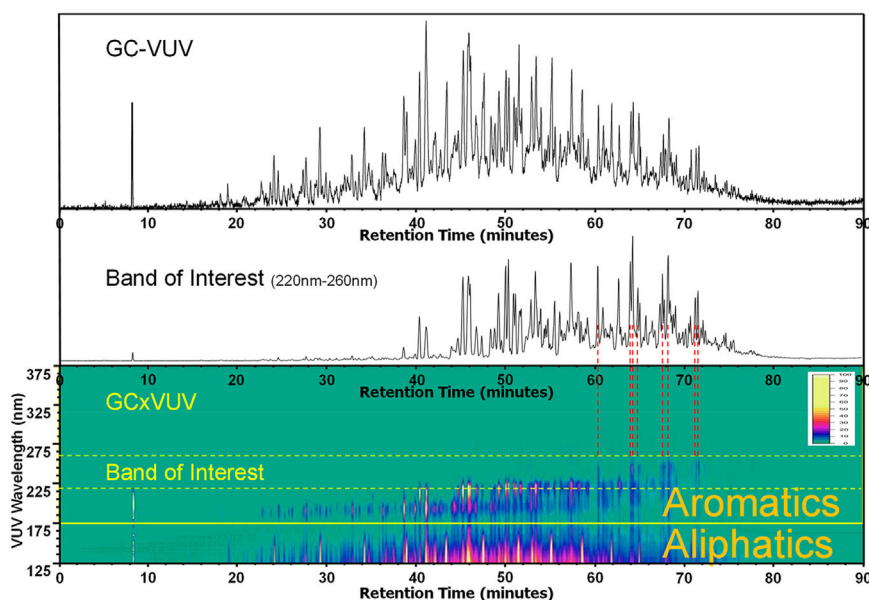


FIGURE 4 An example of three chromatograms. The top is the total absorption by gas chromatography (GC)-vacuum ultraviolet spectroscopy (VUV). The middle is a chromatogram focusing only on the 220 to 260 nm range. The bottom is a three-dimensional representation of the total absorbance. When specifically looking for alkylated triaromatics (which mainly absorb at 220 to 260 nm), their contribution becomes easily seen when using the three-dimensional visualization.⁵³

A limitation of the GC-VUV detector is the relatively small size of the spectral library that has been amassed (<2000 unique compounds, currently). The library's modest size can limit the detector's effectiveness in petroleum analysis, particularly for higher carbon number products. A recent study by Mao et al. used computational chemistry to simulate different hydrocarbon class absorption spectra to help address this issue.⁴¹ The classes simulated were the main classes for petroleum analysis (PIONA). The simulations were performed using

time-dependent-density functional theory to determine absorption energies and probabilities for different compounds. The simulated spectra were then artificially broadened using Gaussian functions to more closely resemble experimental spectra. Simulation of spectra is beneficial for the large carbon number compounds found in fuel, as isolation of these compounds is complex, making it difficult to obtain pure absorbance spectra. Spectral simulation will continue to evolve and contribute to petrochemical analysis; obtaining pure standards

for high carbon number compounds for the population of a library is a formidable challenge, which can be aided using spectral simulation tools. The simulation methods will need to be further refined to improve their accuracy of prediction.

While not directly related to fuels, plug-in software for GC×GC-VUV detection has been created to assist in the qualitative and quantitative interpretation of VUV data.⁵⁴ As previously stated, GC×GC is a crucial technique in group-type analysis of fuels, and the benefits of a free plug-in designed for GC×GC-VUV can significantly decrease the time spent analyzing the data while increasing the amount of information one can extract.

4 | APPLICATIONS OF GC-VUV TO TRADITIONAL AND ALTERNATIVE FUELS

The seminal paper introducing GC-VUV as an analytical technique used gasoline to demonstrate the detector's capabilities.¹⁹ Different absorption spectra were shown for the different compounds, specifically ethanol, paraffins, and aromatics. The use of the detector for differentiating isomers was also exhibited, specifically for xylenes and naphthols. While different analytes were shown, the authors featured fuel and petroleum analysis applications, an area where GC-VUV has provided significant advantages.

Historically, traditional analysis, like detailed hydrocarbon analysis (DHA), struggles with the higher carbon number compounds.⁴⁶ VUV is less limited in this application and has demonstrated the ability to assist in group-type analysis because each class produces different absorbance spectra. For example, the absorbance spectra for olefins tend to peak before 180 nm, while paraffins tend to peak below 120 nm and slowly lose absorption around 165 nm.⁵⁵ An example of the different PIONA classes and their common absorption spectra are shown in Figure 5. The different hydrocarbon group types can access different transition states. Paraffins, for example, only exhibit $\sigma \rightarrow \sigma^*$ excitations, while aromatics can have $\pi \rightarrow \pi^*$ transitions. Regarding paraffins, their exclusive $\sigma \rightarrow \sigma^*$ transitions can cause their absorbance spectra to be quite similar. Nevertheless, these absorption spectra are still unique and can be used to differentiate between different alkanes, including cyclic, branched, and linear hydrocarbons, up to modest carbon numbers (approximately C13).⁴²

The spectral library is currently a limiting factor for applying VUV detection to the full spectrum of compounds encountered in petroleum analysis. Standards for higher hydrocarbons are difficult to obtain, limiting their addition to the spectral library. Larger hydrocarbon molecules can also exhibit mixed functionality; for instance, an aromatic molecule with olefin or extended alkyl branching. Differentiating these compounds becomes more complicated using VUV because the absorption features are additive and overlap to a certain extent. Future research into these larger compounds must be performed to understand how to characterize higher hydrocarbons with mixed functionality.

4.1 | Natural gas and gasoline

A study examining permanent gases, including different sources of natural gases, was one of the first applications of GC-VUV reported.⁵⁶ Natural gases mainly consist of methane but can also contain hydrocarbons ranging from C₂ to C₁₀. The two types of natural gas are biogenic, produced from bacterial metabolism, and thermogenic, produced from geological processes. These types of natural gas can be differentiated based on the differences in their composition of saturated hydrocarbons from C₂-C₄. The standard method to determine the natural gas composition has been to use GC with a thermal conductivity detector to assess the nitrogen, carbon dioxide, and light hydrocarbons, while a flame ionization detector was used for the heavier hydrocarbons. Figure 6 shows an example GC-VUV chromatogram with representative spectra used to identify components in natural gas samples. The authors also applied the technique to drinking water and found that the natural gas contaminating a collected groundwater sample was from thermogenic origins. The benefits of the GC-VUV were that all components of interest could be measured at once, providing a broader detection profile with the addition of qualitative information relative to other techniques. A potential drawback is the need to bring the sample to the laboratory for measurement.

Further application to gas analysis was expanded in a study using a monolithic silica-based column directly connected to the VUV detector.⁵⁷ The light hydrocarbons were a mixture of methane, ethane, carbon monoxide, and carbon dioxide and were fully separated within 15 s. The separation speed was possible due to the deconvolution of coeluting species using the VUV detector. Quantitation of all gases occurred to determine the gas composition within a concentration range of one percent, although special considerations had to be performed to counteract band broadening and increase instrument sensitivity.

Two additional studies examined the ability of VUV detection to identify compounds, specifically individual isomers.^{58,59} The first focused on alkylbenzenes, which are of note in forensics analysis, as they can be used to assist in arson investigations.⁵⁸ Gasoline is the primary accelerant used by arsonists, and the presence of C3-alkylbenzenes allows investigators to conclude that gasoline was used to start a fire. The VUV detector was chosen specifically for this application due to its speed and specificity. When GC-MS is used, the identification of alkylbenzenes is focused more on retention time than the detector directly identifying the compounds. The primary MS detector forensic laboratories have are single quadrupole mass analyzers with an EI source. Identification of the C3-alkylbenzenes would ideally require a prominent molecular ion with several mass fragments. However, the C3-alkylbenzenes do not exhibit molecular ions and generate few unique fragment ions; thus, retention time or retention indices are used as the primary identifier. This limits confidence in qualitative analysis and their chromatographic separation requires long GC columns and slow temperature gradients. When comparing VUV and MS, the ability to differentiate between isomers is vital for arson investigations, specifically for certain alkylbenzenes

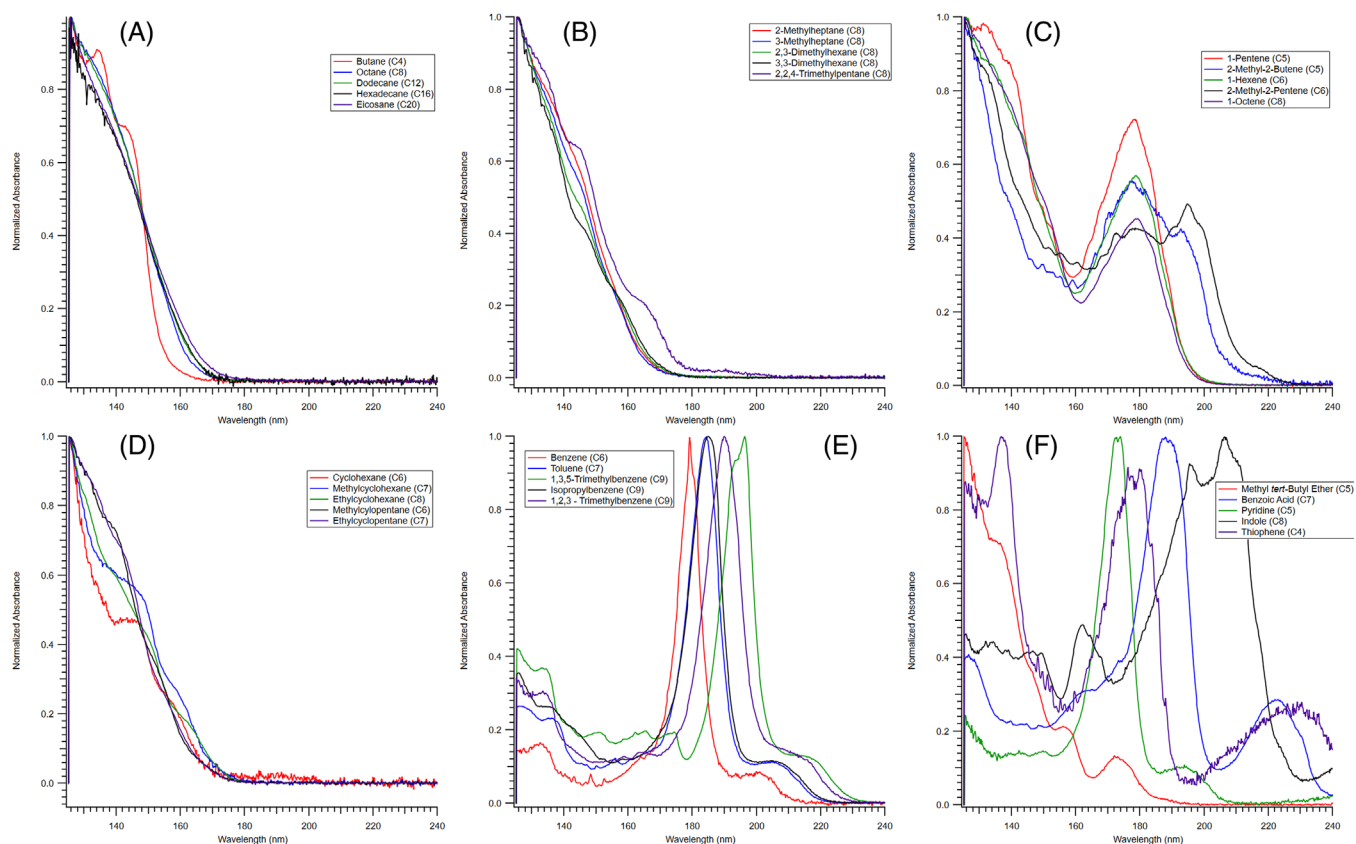


FIGURE 5 Examples of normalized absorbance spectra of the PIONA species. Data were from the library provided by VUV Analytics. Each shows five common examples of (A) paraffins, (B) isoparaffins, (C) olefins, (D) naphthenes, (E) aromatics and (F) oxygenates.

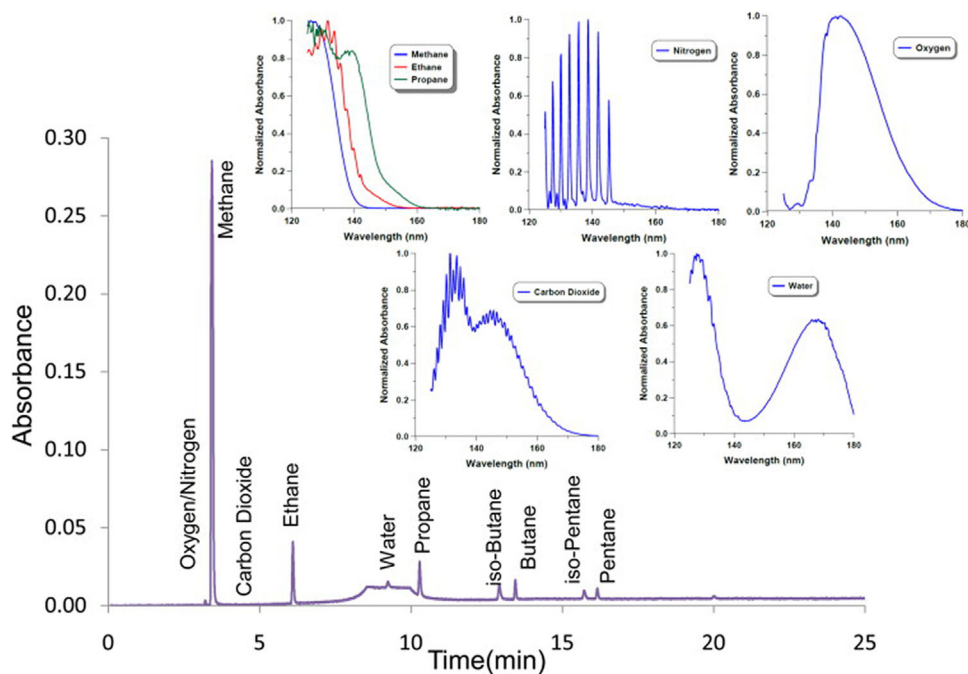


FIGURE 6 A labeled gas chromatography (GC)-vacuum ultraviolet spectroscopy (VUV) chromatogram of a natural gas standard using the absorption from 125 to 240 nm. Representative absorption spectra are also provided, which helped identify the different analytes.⁵⁶

like 1,3-dimethylbenzene and 1,4-dimethylbenzene. Regarding homologous series, VUV could differentiate between homologous series due to a constant shift in the absorbance spectra. MS could also identify species in a homologous series based on the observance of molecular ions.

Another study sought to understand the potential for VUV detection to identify every C_8H_{18} isomer.⁵⁹ Standards for all eighteen octane isomers were obtained and measured, and their spectra were added to the library. Complex mixtures of multiple hydrocarbons were created, and the temporal area where octane was expected to elute was examined. Software unambiguously identified every C_8H_{11} isomer down to < 0.40% by mass. When a researcher assisted in interpreting the data, every isomer was identified down to approximately 0.20% by mass. Both studies showed that while GC-VUV can focus on assigning PIONA classes to every compound, VUV was also capable of targeted analysis.

4.2 | Diesel and other middle distillates

Middle distillates include fuels such as diesel (gas oil), jet fuel, and kerosene.⁴ These are complex samples where the number of carbons ranges from approximately C_8 to C_{24} and include a boiling point range of about 180 to 375°C (See Table 1).⁶⁰ Middle distillates are an essential energy source. However, their complexity is significantly increased relative to lighter distillates. GC-VUV, with its ability to differentiate isomers, and its combination with TID, has been used for characterizing middle distillates.

One of the first studies of GC-VUV examining middle distillates was the determination of hydrocarbon group types in diesel fuel.⁶¹ Chromatographically, an ionic liquid column was utilized to separate saturates and the mono-, di-, and polyaromatics from each other. Spectral filters were then applied to the overall absorption spectra. These filters were created from the specific wavelengths that correlated to specific compounds. Spectral filters can increase specificity for certain compound classes, such as aromatics, due to their longer wavelength absorptivity, which is lacking for saturated hydrocarbons. Detection and error rates were compared to supercritical fluid chromatography (SFC). The GC-VUV data agreed well with that from SFC, except for some minor differences. SFC showed that two specific fuels compared were quite different, while VUV showed that the two types of diesel were essentially the same. This disagreement was rationalized with the conclusion that the GC-VUV interpretation was more robust, based on its ability to provide spectral absorption data combined with the chromatographic output.

In another early study, Schenk et al. emphasized the benefits of spectral deconvolution provided by GC-VUV.⁴⁵ A specific focus was placed on the characterization of dimethylnaphthalenes, which can be present in significant levels in diesel and jet fuel. Dimethylnaphthalenes are particularly challenging to differentiate using GC-MS due to their significant coelution and similar mass spectra. Different ratio mixtures of eight overlapping dimethylnaphthalene isomers were used to test the accuracy, precision, and sensitivity of the GC-VUV detec-

tor for identifying these compounds. It was found that a mixture of dimethylnaphthalene isomers could be deconvolved to determine individual component concentrations for up to two orders of magnitude (99:1) difference in their relative abundance, within reasonable error. This ratio is still recommended for deconvoluting species exhibiting high spectral similarity. When spectra are dissimilar, much larger disparities in the relative abundance (e.g., > 1000:1) of coeluting species can be accommodated. For the characterization of the fuels, different spectral filters were used to focus on differentiating the saturates (125 – 160 nm) from unsaturated components (170 – 240 nm). Different mono-, di-, and trimethylnaphthalenes were also accentuated using a 210 – 220 nm spectral filter. Not only did this study establish reasonable bounds for deconvoluting highly similar species, such as dimethylnaphthalenes, but it also established the benefits of using different filters to gain a greater understanding of what is present in middle distillate fuels.

As middle distillates are well studied, comparing the VUV detector to traditional detectors like GC-FID and GC-MS was essential. Two studies examined GC-VUV versus these other detectors using middle distillates. In an early study, a comparison was performed between GC-VUV, GC-FID, and GC×GC-MS.⁶² The study focused on comparing GC-VUV to the traditional methods for determining common chemical markers used to identify the age and source of commercial weathered and unweathered diesel fuels. The different methods were in good agreement. It was proffered that the GC-VUV might find a valuable place in environmental forensics and associated litigation, as an absorbance detector is easier to understand for the average person, compared to mass spectrometry and the use of advanced multidimensional separation techniques. Standard methodologies would need to be established to reach such a point.

A separate study compared GC-VUV to different separation strategies and detectors involved with DHA and GC×GC analysis for mixed hydrocarbon streams.⁴⁶ Mostly, there was good agreement between GC-VUV, DHA, and GC×GC methods. All three methods provided PIONA analysis with an relative standard deviation (RSD) value of 1.3% or lower when injected five times a day over 3 days. There were also clear benefits of GC-VUV, as it could identify compounds that DHA could not. Specifically, DHA (using a flame ionization detector) misidentified a combination of isoparaffins and naphthenes as C_9 -olefins. Their true identities became apparent when looking at the VUV spectral data. Instrument software was used to perform TID to quantitate the compounds, and the result provided agreement within 0.6% of the actual levels reported for the sample using traditional methods. The GC-VUV approach was also much faster than the alternative methods.

4.3 | GC-VUV and pyrolysis oils

It is generally accepted that the use of traditional fossil fuels as a primary energy source has caused lasting environmental effects.⁶³ As such, the development of alternative fuel sources is currently an active area of research. One strategy is the creation of fuels through the pyrolysis of plant matter and plastic waste.^{64,65} Pyrolysis is the

process of using heat in an enclosure without oxygen to decompose matter. During this process, which occurs from below 400°C to above 1000°C, the matter is chemically converted into oils, and the resulting oil created from the pyrolysis process can be further refined into functional products, such as fuels.⁶⁶ The generated pyrolysis oils are exceptionally complicated, as the feedstocks from which they are derived can be highly variable in their compositions.⁶⁷ Multiple studies have been conducted using gas chromatography to characterize different types of pyrolysis oils, mainly those generated from biomatter and plastic waste.⁶⁸ Pyrolysis oils can be more complicated than petroleum, and the added spectroscopic absorption information provided by GC-VUV can benefit their characterization.

Although limited investigations have been reported on the topic, Dunkle et al. used GC-VUV to provide qualitative and quantitative data on the hydrocarbon composition of mixed waste plastic pyrolysis oils.³⁸ An in-house spectral library was created to identify and quantify the different pyrolysis oils with a detection limit of 0.1 percent weight. Hydrocarbons were accurately evaluated from a range of C₄ to C₃₀₊. The principal findings were that the paraffin and isoparaffin content was much lower in plastic waste pyrolysis oil than in conventional hydrocarbon streams. They also found that the olefin content in the studied pyrolysis oils was much higher than in petroleum. It is not uncommon for olefin content in pyrolysis oils to range from 35 to 65 weight percent, much higher than the <1% olefin content traditionally found in samples from petroleum sources. GC-VUV was preferred over traditional DHA using GC-FID, as the GC-VUV method was more accurate for identifying and quantifying the different hydrocarbon classes and exhibited similar repeatability.

5 | SUMMARY AND OUTLOOK

GC-VUV, a relatively new technique, has shown promise for the characterization of fuels and petroleum products. Its primary focus has been the middle distillates, where the complicated nature of the mixture suits the detector's abilities. While GC-VUV has been used to study many different fuel types, there is a lack of GC-VUV studies for alternative fuel sources, like pyrolysis oils.

With all the benefits of the VUV detector, there is still room for improvement. The first concern is a relatively modest limit of detection. While the VUV can detect analytes in the low parts per million concentration, many other common GC detectors are more sensitive. Newer generations of VUV detectors have improved sensitivity, increased the spectral range of absorption that can be acquired (125–420 nm), and added high-temperature capabilities (up to 430°C). A modest library of compounds is currently available to users. While VUV can identify and deconvolute peaks, a limited library can affect the performance of certain applications, like those products with high carbon number hydrocarbons.

VUV detection is a powerful technique that can be used to complement traditional GC detection techniques, such as FID, MS and others. Its straightforward use and ability to deconvolute peaks pro-

vide qualitative and quantitative data, and separate isomers make it a formidable tool in support of petroleum and pyrolysis oil analysis. VUV can be paired with other detectors with a more extensive library or that can differentiate homologous series easier or have a lower limit of detection. As the GC-VUV becomes more integrated into more laboratories, its capabilities and range of applications will continue to be expanded. Further establishment of standard methods, such as those propagated by ASTM, will also increase its rate of adoption.

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CONFLICT OF INTEREST STATEMENT

Dr. Kevin A. Schug is a member of the scientific advisory board for VUV Analytics, Inc. The other author declares no conflict of interest.

DATA AVAILABILITY STATEMENT

This is a review article and has no associated data.

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