Gas Chromatography - Vacuum Ultraviolet Spectroscopy: A Versatile Tool for Analysis of Gasoline and Jet Fuels

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Gas chromatography (GC) is a powerful analytical tool, particularly in the petrochemical industry. Current fuels analysis is performed using a variety of GC methodologies, including detailed hydrocarbon analysis (DHA) and multidimensional GC for gasolines, as well as fluorescent indicator adsorption (FIA) for both gasoline and jet fuels. However, these methods have several drawbacks, including long run times, complex configurations, and, in the case of FIA, grave concerns over the quality of the materials required to perform the analysis.

Vacuum ultraviolet (VUV) spectroscopy is a relatively new analytical methodology that utilises molecules' unique spectral absorbance fingerprints in the vacuum ultraviolet wavelength range (125-240 nm) to identify and quantitate analytes. Using a single hardware configuration, GC-VUV can perform PIONA-class quantitative analysis - including speciation of conjugated dienes - in gasoline samples, as well as measure total saturates, aromatics, and di-aromatics in jet fuel samples.

1. Introduction

Characterisation of petroleum products, from liquefied petroleum gases (C_1-C_4) to gasoline (C_5-C_{12}) to middle distillates like jet fuel and diesel (C_{10}-C_{20}) and even the heavier oils and waxes (C_{20}+) is one of the highest priorities for refiners. They must not only comply with various government-instituted environmental and public safety regulations but also constantly gain advantages over their competitors. In the downstream refining sector, determining fuel content can help refine process procedures and streamline quality control of their finished fuels [1, 2].

Since the early 1950s, GC has been the primary tool for analysing fuels. In the ensuing 70 years, many different detector types, foremost among them flame ionisation detection (FID) and mass spectrometry (MS), have been used with gas chromatography to determine boiling point distribution, hydrocarbon class type, and, in certain cases, even speciation of petroleum products [3]. Current PIONA methods class most gasoline components into one of five hydrocarbon group types: paraffins (linear alkanes), isoparaffins (branched alkanes), olefins (alkenes), naphthenes (cycloalkanes), and aromatics.

While many of the current analytical methods are widely accepted as 'gold standards', technologies and methods are constantly being improved and updated. The most common shortcoming most GC methodologies experience is long run times. Petroleum samples are some of the most complex matrices: gasoline contains hundreds of compounds, and some of the higher-carbon cuts can contain thousands. Most detectors cannot provide any qualitative information of eluting analytes, requiring baseline separation of peaks to obtain the most accurate data. Even those detectors that can identify compounds (e.g., mass spectrometry) are flow-limited, and deconvolution software is not entirely reliable.

VUV spectroscopy is a relatively new GC detection methodology that combines qualitative spectral identification - similar to mass spectrometry - with faster flow rates, allowing for shorter run times while still maintaining high accuracy and precision. This paper details several GC-VUV petrochemical applications that are impacting the petrochemical industry.

2. Current Analysis of Fuels

2.1. Detailed Hydrocarbon Analysis

Detailed hydrocarbon analysis (DHA), under the ASTM D6730 method, is a widely utilised methodology for gasoline-range fuels analysis. This method purports speciation of up to 600 compounds, though not all are named. It employs a 100-meter 100% poly-dimethylsiloxane (PDMS) column - with a 5% diphenyl PDMS 'tuning' precolumn - connected to a flame ionisation detector (FID), a cryogenic starting oven temperature (5°C), and a run time of 174 minutes to maximise baseline separation of analytes, allowing for a high degree of speciation for PIONA compounds and select oxygenates [4]. The method has since been refined and the run time shortened, down to as low as 38 minutes in some cases.

The major drawback of DHA is that it relies solely on peak retention time for identification, since FID response does not provide any qualitative information of its own. The 'tuning' precolumn is necessary to help provide baseline separation (R_s > 1.5) of known coelutions like benzene/methylcyclopentene and m-xylene/p-xylene. Also, any unexpected coelutions cannot be quantified, since the interfering compound(s) cannot be identified [5].

2.2. Multi-Dimensional Gas Chromatography

Multi-dimensional GC-FID, under the ASTM D6839 method and the trade name 'Reformulyzer' from PAC International, measures paraffins (alkanes), olefins (alkenes), naphthenes (cycloalkanes), and aromatics (PONA) compounds (paraffins and isoparaffins are not separated) and oxygenates in gasoline and gasoline blend streams [6]. While this method touts a 39-minute run time, the setup is extremely complex. A single system contains 4 different columns, each with a unique stationary phase, as well as a hydrogenator, 3 separate traps - alcohol, olefin, and EAA (ether-alcohol-aromatic) - all connected via 7 valves, with temperature controllers for each component. With multiple columns and connections, there is a greater chance for leaks or restrictions, and instrumental problems take longer to troubleshoot and repair, leading to longer periods of down time.

2.3. Fluorescent Indicator Adsorption

Perhaps one of the oldest fuels analysis methods still in use today is fluorescent indicator adsorption (FIA). FIA was developed in the 1940s and approved as ASTM method D1319 in 1954, and it is still the primary test method for measuring saturates, olefins, and aromatics in gasoline, jet fuel, and diesel. Fuel samples are physically separated using silica gel fractionation, and the length of each cut, marked by fluorescent dyes, is measured with a ruler [7]. However, the boundaries between the cuts are not always clean, and manual measurement adds a level of human error to the analysis.

Recently D1319 has come under serious scrutiny: the most recent batch of dyes do not fluoresce properly in the aromatics region, which is particularly troublesome for jet fuel and diesel, as aromatics comprise up to 30% of the total volume. Furthermore, the sole manufacturer of this dye no longer exists, and so far, alternate syntheses of the dye have been unsuccessful. Current alternative methods include ASTM D5186 and D6379, which use supercritical fluid chromatography (SFC) and high-performance liquid chromatography (HPLC), respectively.

2.4. UV Spectrophotometry

Naphthalenes, which contribute heavily to soot formation during combustion, are monitored in jet fuel using ultraviolet (UV) spectrophotometry (ASTM D1840), a method developed in the early 1960s. Fuel samples are diluted and their total absorbance at 285 nm is measured [8]. However, this method cannot give any qualitative information on the sample, and its low absolute absorbance can lead to a relatively large error range. Additionally, non-naphthalene di-aromatics (e.g., dibenzothiophenes, biphenyls) and tri-aromatics are known to interfere with accurate measurements, as these compounds also have UV absorbance at 285 nm.

2.5. Maleic Anhydride Method

The original method for determining conjugated diolefins in fuels (and one that is still in use today) is UOP326, also known as the maleic anhydride method. Originally developed in 1965, this method uses maleic anhydride as a dienophile in a Diels-Alder reaction with conjugated diolefins in the sample. Excess maleic anhydride is added to the sample and heated in a reflux for 3 hours; the remaining maleic anhydride is then converted to maleic acid and measured by colorimetric titration [9].

Although UOP326 is still used today in some capacity, it has several drawbacks. The method takes over 3 hours, whether done manually or automated. Certain nucleophiles like alcohols and thiols (which are commonly found in or added to fuels) will also react with maleic anhydride, positively skewing values. Conversely, some sterically-hindered diolefins like 2,5-dimethyl-2,4-hexadiene will not react at all, negatively skewing values. Because of this lack of selectivity, the method is only semiquantitative and cannot give qualitative information, particularly which diolefin species are present.

More recently, an assortment of other methodologies for measuring conjugated diolefins have been implemented, including derivatised-sample GC-MS or GC-nitrogen chemiluminescence detection (NCD), HPLC, SFC-UV, nuclear magnetic resonance (NMR), near infrared (NIR) spectroscopy, and voltammetry [10].

3. Vacuum Ultraviolet Spectroscopy Theory

VUV absorption spectroscopy is a new addition to the field of analytical chemistry, though the concept of measuring in this spectral region has been used in synchrotrons for decades. Traditionally this type of spectroscopy required a vacuum environment to properly analyse samples, as atmospheric molecules like water and oxygen absorb in this wavelength region and thus interfere with measurements. However, the GC-VUV detectors from VUV Analytics overcome this problem by keeping the optical and detector environments under a positive pressure of an inert gas such as nitrogen or helium, eliminating potential atmospheric interferences.

Photons in the 'vacuum ultraviolet' spectral region (i.e., 125-240 nm) are absorbed by a molecule's electrons depending on the molecular orbital transition and the energy required to bridge that HOMO-LUMO gap. Higher energy, lower wavelength photons will cause transitions between the sigma bonding (σ) or non-bonding (n) orbitals and the sigma anti-bonding (σ^*) orbitals; lower energy, higher wavelength photons cause transitions between pi bonding (π) and pi anti-bonding (π^*) orbitals. Most molecules have at least a single sigma bond, which means nearly all molecules absorb in this wavelength region. Furthermore, because each molecular orbital has a specific position in three-dimensional space, each molecule probed by VUV light will have a unique spectral absorbance across the wavelength range, sometimes referred to as a 'spectral fingerprint' [11, 12].

Quantitation using VUV spectroscopy is straightforward, as it follows the Beer-Lambert Law (absorbance linearly proportional to concentration), akin to other light spectroscopy techniques. First-order quantitation means coelutions can be linearly deconvolved with a high degree of accuracy. This allows the chromatography of GC-VUV to be deliberately compressed, leading to significantly shorter run times [5].

4. GC-VUV Fuels Applications

4.1. PIONA Analysis of Gasoline (ASTM D8071)

ASTM D8071 was officially approved in 2017 as a test method for determination of hydrocarbon group types, along with several select hydrocarbons and oxygenates, in gasoline-range fuels using GC-VUV. Most analytes are classed into one of the five PIONA hydrocarbon group types. Certain specific analytes are called out individually: the octane boosters methanol, ethanol, and isooctane, and light VOCs such as BTEX (benzene, toluene, ethylbenzene, and xylene isomers), naphthalene, and the methylnaphthalenes [13].

This method utilises a single 30-meter 100% PDMS GC column for its 33.6-minute analysis, compressing the chromatography

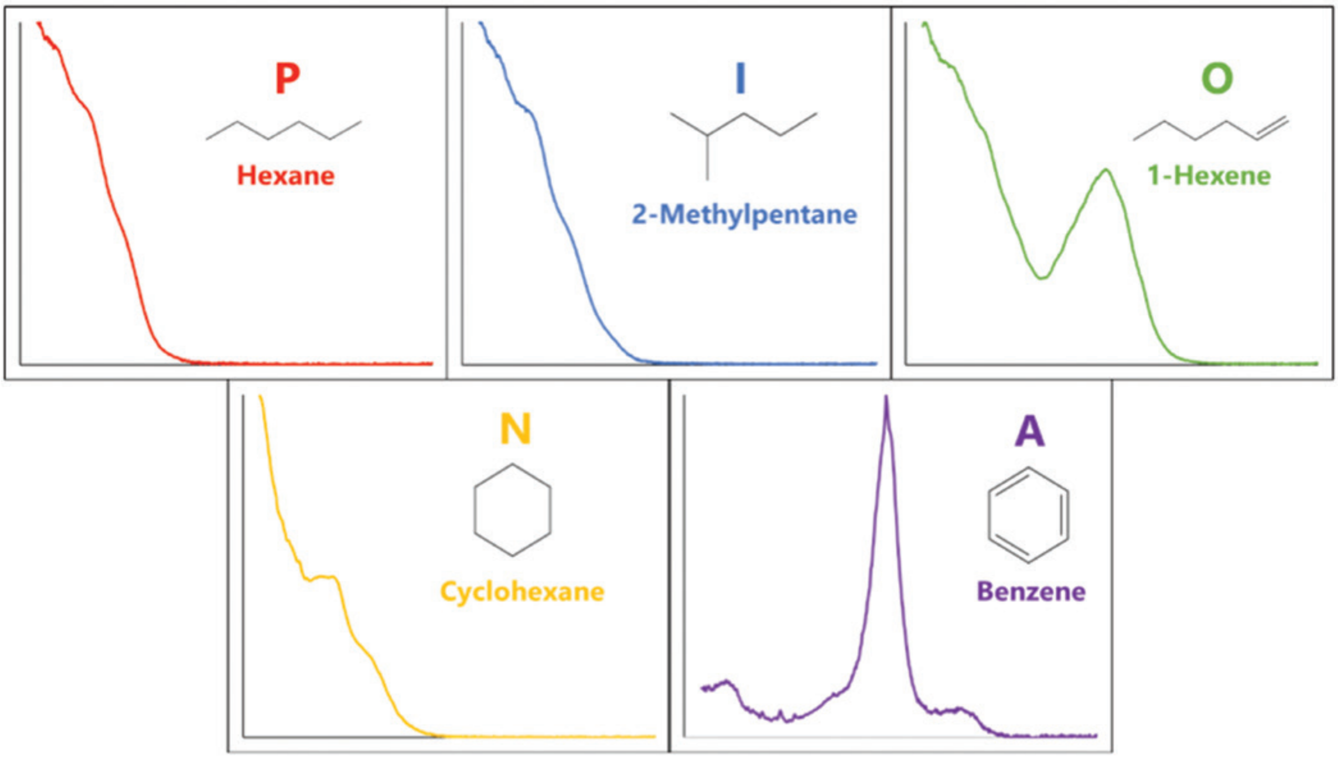


Figure 1: VUV absorbance spectra from 125-240 nm for C_6 compounds of each of the PIONA hydrocarbon class types. The shapes of these spectra are representative of their respective class across the gasoline range.

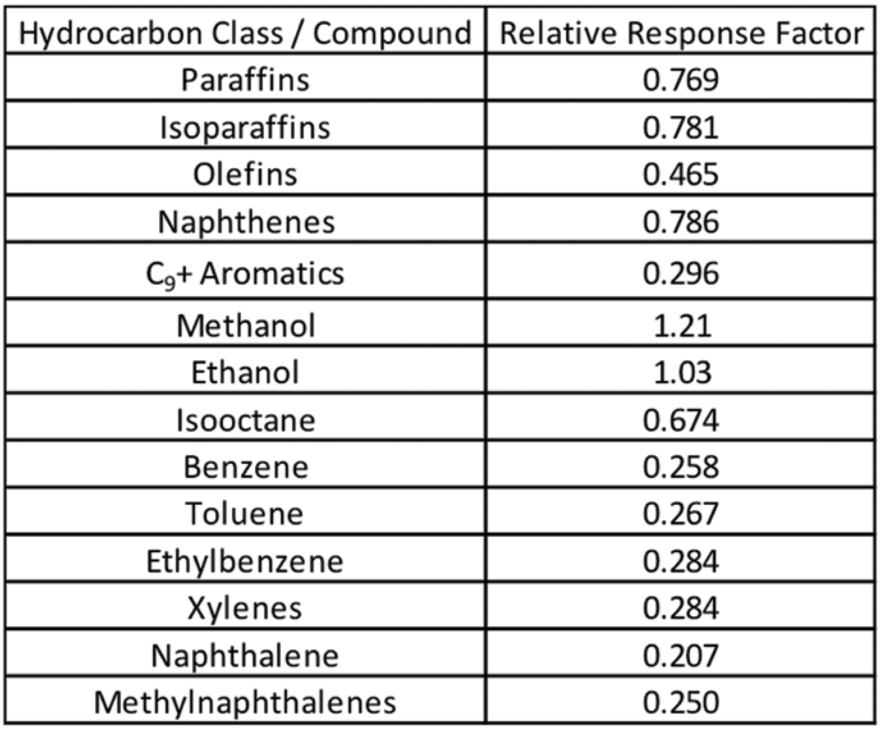
and relying heavily on VUV's ability to spectrally deconvolve coeluting analytes and quantitate by hydrocarbon class and carbon number during the data processing step (Figure 1).

Data is analysed using a novel automated quantitative method, time interval deconvolution (TID)[14]. Unlike a typical chromatographic quantitative analysis which sets quantitation windows in which a peak is measured in some capacity, TID divides the entire chromatogram into equal time segments, typically 0.02 minutes wide. For each time interval, the spectra within that interval are summed, and the summed spectrum is matched against the spectral library (approximately 770 compounds) for the best combination of 1 - 3 spectra (called a tiered search), depending on whether the addition of the second or third component improves the fit metric by a defined amount. In order to speed up the analysis, a given time segment is searched within a user-defined retention index (RI) window (typically ± 25 RI units) in the library [14, 15].

Using this iterative process, the total spectral response for each class/analyte is determined. Quantitative data are calculated without the need for calibration standards. Instead, relative response factors are used to calculate percent mass: for each PIONA class, an experimentally determined average response factor is used; for the individual target analytes, an experimentally determined response factor specific for that analyte is used (Table 1). Further conversion can be made to percent volume using either a class-based average density or an analyte-specific density.

This method operates with a high level of precision. Four ASTM gasoline proficiency samples were run 12 times each and analysed for each PIONA class as well as 9 targeted analytes. All %RSD values are below 6%, with all but four values below 2.5% (Table 2).

Table 1: Relative response factors for the PIONA hydrocarbon classes and select speciated compounds.



Hydrocarbon Class / Compound	Relative Response Factor
Paraffins	0.769
Isoparaffins	0.781
Olefins	0.465
Naphthenes	0.786
C_9+ Aromatics	0.296
Methanol	1.21
Ethanol	1.03
Isooctane	0.674
Benzene	0.258
Toluene	0.267
Ethylbenzene	0.284
Xylenes	0.284
Naphthalene	0.207
Methylnaphthalenes	0.250

Table 2: Precision of D8071 analysis run on four gasoline samples, with 12 runs per sample. All %RSD values are below 6%, and most are below 2.5%.

Hydrocarbon Class / Compound	% RSD - Sample 1	% RSD - Sample 2	% RSD - Sample 3	% RSD - Sample 4
Paraffins	1.2	0.83	0.52	0.59
Isoparaffins	0.26	0.35	0.39	0.96
Olefins	1.1	1.4	4.0	1.7
Naphthenes	5.9	3.9	1.3	2.3
Aromatics	0.36	0.46	0.21	0.56
Ethanol	0.37	0.25	--	0.46
Isooctane	0.47	0.41	0.75	0.89
Benzene	0.63	0.94	0.56	0.81
Toluene	0.34	0.34	0.26	0.62
Ethylbenzene	1.1	0.28	0.51	0.57
Xylenes	0.38	0.37	0.54	0.74
Naphthalene	0.83	0.71	0.32	0.83
Methylnaphthalenes	1.9	5.0	0.56	1.4

4.2. Conjugated Diolefins Analysis

Though not officially within the scope of ASTM D8071, conjugated diolefins can be analysed using the same GC-VUV acquisition method as D8071, in fact using the same quantitative analysis as well. The conjugated diolefins are spectrally distinct from any of the saturates, as well as the olefins and mono-aromatics, in that they have good absorbance past 200 nm (Figure 2). This makes the spectral deconvolution rather straightforward (Figure 3). Detection limits for the C_5-C_8 conjugated diolefins range from 0.01-0.05% mass, with isoprene (2-methyl-1,3-butadiene) having the lowest detection limit.

4.3. Verified Hydrocarbon Analysis

Verified hydrocarbon analysis, or VHA, is a GC-VUV analogue of the DHA method ASTM D6730. This method was initially developed using similar conditions to D6730, which includes a 100-meter column and a cryogenic (5°C) oven start but no precolumn, as the critical separations like benzene and methylcyclopentene can be done spectroscopically. Eventually the method was translated to a 60-meter column in order to reduce run time while still maintaining good separation and similar elution order, reducing the run time from 174 minutes to 49 minutes. Currently the method reports up to 151 compounds by both mass and volume percent, and more compounds are being added to the spectra library. These 151 compounds account for approximately 90% of all gasoline components, giving good coverage across the hydrocarbon classes and carbon number (from C_3 to C_{15}).

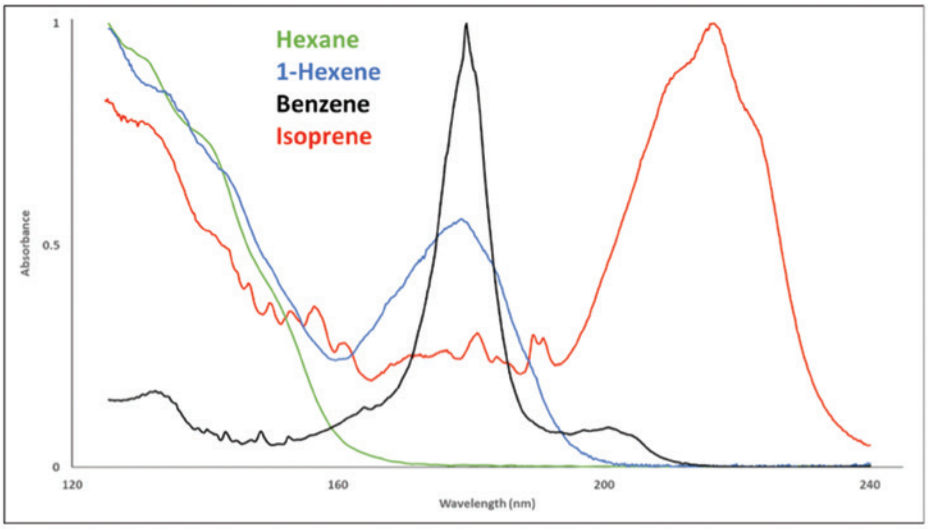


Figure 2: VUV absorbance spectra of several hydrocarbon species. The selective VUV absorption in the 200-240 nm region for the conjugated diolefin isoprene (2-methyl-1,3-butadiene) makes it spectrally distinct from any of the PIONA spectra.

Table 3: Comparison of D8071 and two VHA methods for gasoline analysis. Both VHA methods correlate with D8071 well, especially the shorter (60m) method.

Hydrocarbon Class / Compound	D8071	VHA (100m)	VHA (60m)
Paraffins	13.7	15.2	13.8
Isoparaffins	27.6	28.5	27.7
Olefins	13.2	12.7	12.3
Naphthenes	8.84	6.37	7.75
Aromatics	25.6	24.8	26.9
Di-Aromatics	0.97	0.859	0.994
Ethanol	10.1	11.5	10.6
Isooctane	1.91	2.08	2.00
Benzene	0.426	0.479	0.441
Toluene	3.51	3.99	3.82
Ethylbenzene	0.875	0.847	0.913
Xylenes	5.55	5.83	5.96
Naphthalene	0.266	0.279	0.345
Methylnaphthalenes	0.590	0.580	0.615

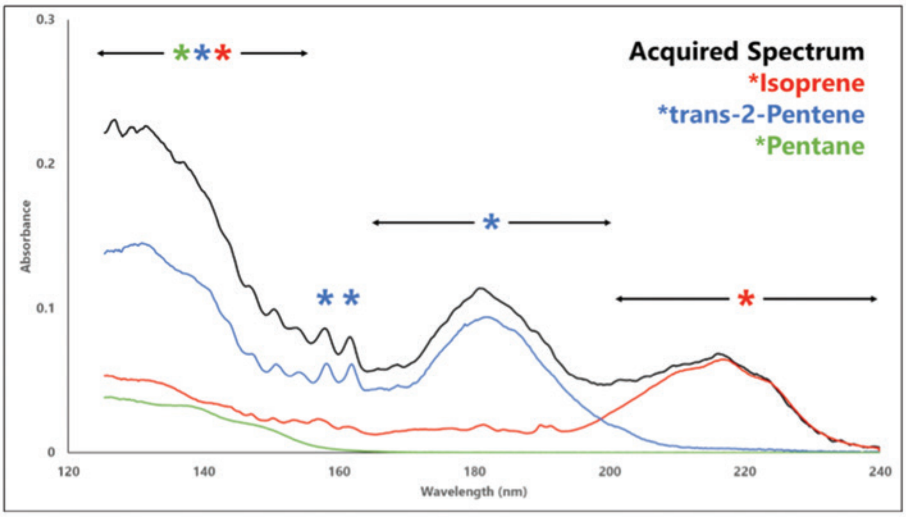


Figure 3: Spectral deconvolution of these coeluting analytes is straightforward, as each compound's VUV absorbance spectrum contributes to different regions of the acquired spectrum (note: asterisk colours correspond to compound name's colour in legend).

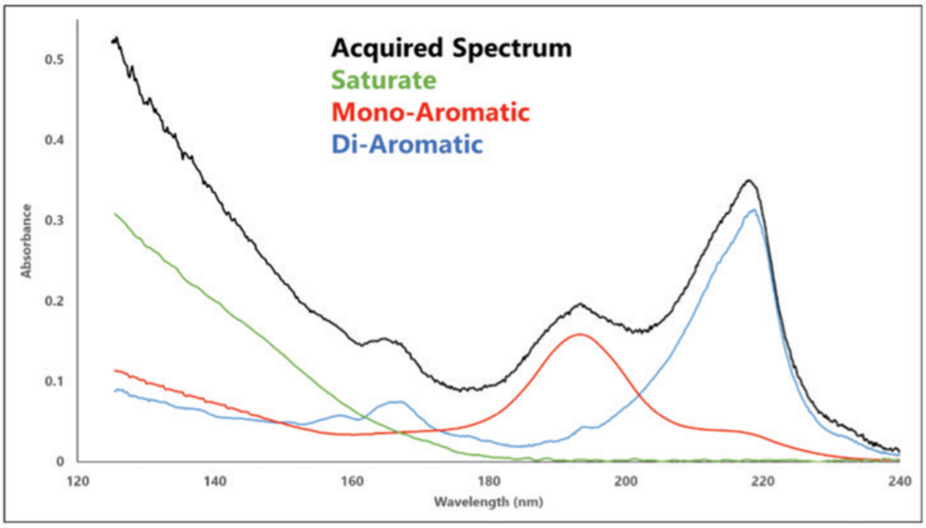


Figure 4: Similar to Figure 3, each hydrocarbon class analysed in the GC-VUV jet method is spectrally distinct, increasing the accuracy of deconvolution during data analysis.

To check the accuracy of this VHA method, a well-characterised gasoline sample was analysed using both the 174-minute and 49-minute VHA methods as well as D8071. Mass percent data of all reported D8071 classes and species were compared for the three methods (individual compound values from VHA analyses were summed to get PIONA values). Both VHA methods compare well to the D8071 values, especially the 49-minute method (Table 3).

4.4. Jet Fuel Analysis by GC-VUV

Until recently, gas chromatography has not played a role in analysis of jet fuels. However, with D1319 no longer viable as the referee method, alternative methods were needed, and GC-VUV seemed a natural fit given its aptitude for analysing gasoline.

Jet fuel is a middle distillate, ranging from C_6 to C_{21}, making it a much more complex matrix than gasoline. As the carbon number increases, the number of possible isomers increases exponentially, cresting well over 60,000 branched-chain isomers by C_{18}. Also, the absorbance spectra of higher carbon-number saturates (starting around C_{10}) become too similar to distinguish. Because of these complexities, speciation is not practical, nor even the PIONA-type class analysis of gasoline. Therefore, the only hydrocarbon groups reported are total saturates and total aromatics, which is further subdivided into total mono-aromatics and total di-aromatics, analogous to data reported by D1319 and D1840.

Olefins, while reported in D1319 and some of the other alternate methods, are typically not present in jet fuel, and no olefins have been positively detected in any jet fuel samples analysed by GC-VUV. The VUV absorbance spectra of olefins have response in both the saturate (125 - 160 nm) and aromatic (170 - 200 nm) regions, which means that any reported olefin values are likely a misidentification of saturate-aromatic coelutions; therefore, olefins are not included in the searchable spectra library.

This method utilises the same hardware configuration as D8071 in a 14.1-minute analysis. The chromatography is compressed to an even greater degree, since the spectral deconvolution in the data analysis must only resolve saturates, mono-aromatics, and di-aromatics, all of which are spectrally distinct (Figure 4).

Initial GC-VUV results for jet fuel analysis correlate favourably with D1319. Ten proficiency samples were analysed using GC-VUV, D1319 (FIA), D5186 (SFC), and D6379 (HPLC-UV). While both the SFC and HPLC methods biased high on every sample for total aromatics, GC-VUV was evenly distributed on either side of the D1319 results, with four results slightly higher than, four slightly lower than, and

Table 4: Precision of GC-VUV jet fuel analysis run on six jet samples, with 8 runs per sample. All %RSD values are below 3.5%, and most are below 1%.

	Total Saturates		Total Aromatics		Total Di-Aromatics	
Sample	Average	%RSD	Average	%RSD	Average	%RSD
1	82.2	0.03	17.8	0.1	1.88	0.1
2	80.9	0.02	19.1	0.1	0.87	0.5
3	87.6	0.02	12.4	0.1	2.11	0.3
4	82.2	0.10	17.8	0.5	1.12	1.2
5	84.4	0.03	15.6	0.1	0.10	3.3
6	86.9	0.03	13.1	0.2	0.99	0.6

two equal to reported D1319 data, and an average difference of only 0.4% volume (Figure 5). For the di-aromatic values, nine of the ten samples showed good correlation with D1840, and while the sample with the highest expected di-aromatic concentration reported high for GC-VUV, both SFC and HPLC reported a similar result (Figure 6).

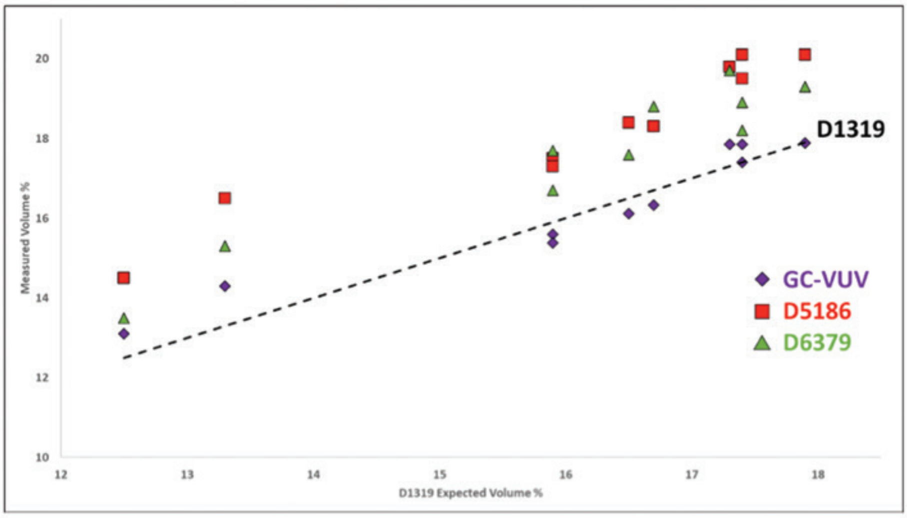


Figure 5: A comparison of measured total aromatics content for 10 jet fuel samples. Note GC-VUV's better correlation to D1319 than the other two methods.

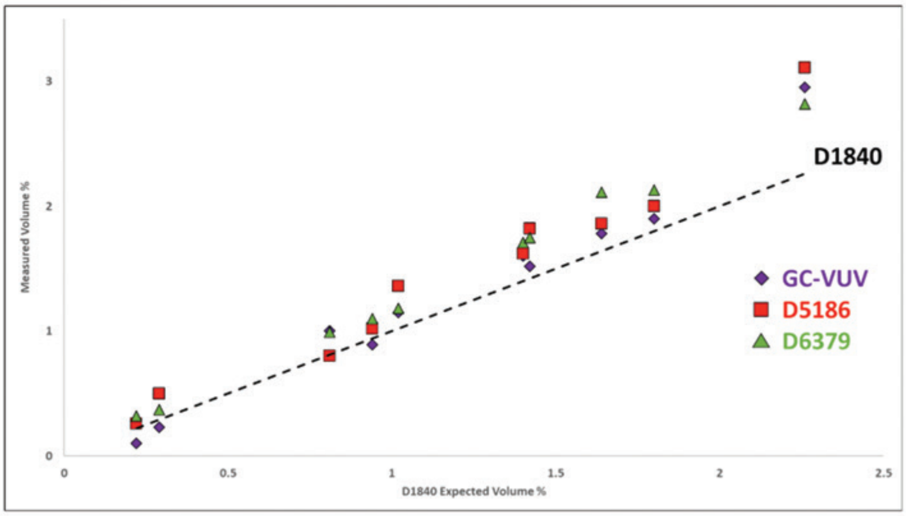


Figure 6: A comparison of measured total di-aromatics content for 10 jet fuel samples. GC-VUV correlates well with both the referee method (D1840) and the alternative methods.

This method operates with a similarly high level of precision as D8071. Six jet fuel proficiency samples were run 8 times each and analysed. All %RSD values are below 0.1% for total saturates, below 0.5% for total aromatics, and below 3.5% for total di-aromatics (Table 4).

5. Conclusions

GC-VUV has quickly become a reputed methodology for analysis of fuels [16]. Applications for both gasoline and jet fuels display good correlation to existing methods with high levels of precision, while reducing run times by up to 80%. Future applications for both lighter (e.g., liquefied petroleum gas) and heavier (e.g., diesel, crude oils) distillation cuts are sure to follow in the wake of the technology's current successes.

In a world where time is money, the data gained from an analysis must be worth the time devoted to acquiring that data, and efficiency is king. As the VUV technology matures, the efficiency of its applications will only continue to grow as it is able to provide more accurate and detailed information in shorter analysis times.

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