The GC-VUV Toolkit

Solutions Guide for
Common GC Headaches

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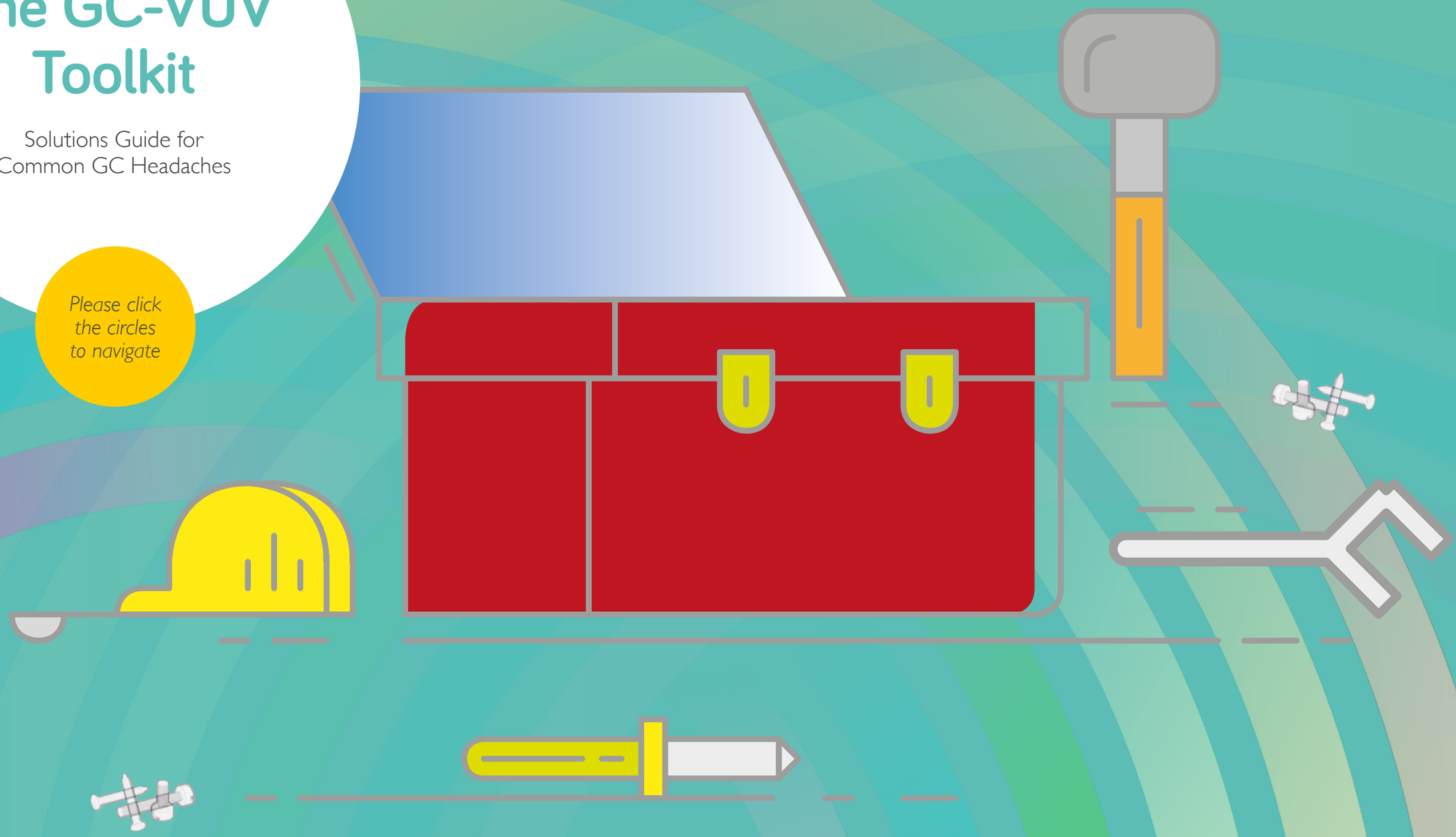


ABSTRACT

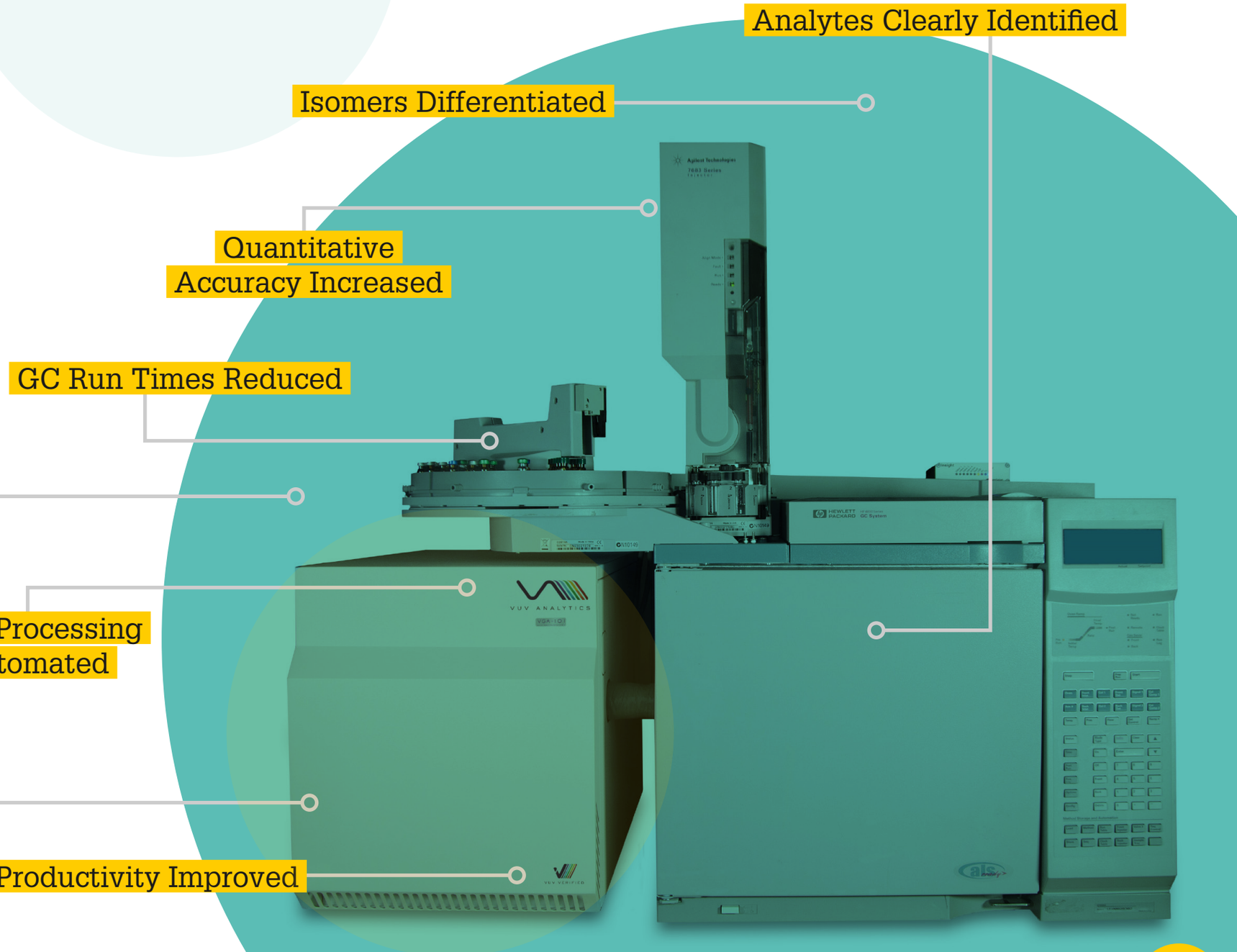
INTRODUCING GC-VUV

THE GC-VUV TOOLKIT

CONCLUSION

Abstract

Gas Chromatography – Vacuum Ultraviolet (GC-VUV) spectroscopy is a recent innovation introduced in 2014 as a universal detection platform for gas chromatography (1). Virtually everything absorbs in the vacuum ultraviolet region (120 – 240 nm) measured by VUV detection. VUV light absorption creates unique spectral signatures in the gas phase that result in unambiguous compound identification and linear quantitative analysis. The unique capabilities inherent to GC-VUV help to solve common gas chromatography problems such as correct isomer identification, poor selectivity, long method run times, analyte co-elution, burdensome data processing and analysis, and method scalability to production environments. What follows is an overview of the GC-VUV toolkit and how it addresses these challenges across a wide spectrum of complex applications.



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Introducing GC-VUV

How VUV Spectroscopy Works

Nearly all gas-phase species absorb and display unique spectra in the vacuum ultraviolet (VUV) region of the electromagnetic spectrum with the exception of hydrogen, helium, and argon. VUV photons probe high energy electronic transitions within this wavelength range including **σ→σ***, n→**σ***, and **π→π***, as shown in Figure 1. This results in spectral "fingerprints" that are specific to analyte electronic structure and functional group arrangement. Unique VUV spectra enable closely related compounds such as structural isomers to be clearly differentiated.

GC-VUV spectral data is inherently three-dimensional (time, absorbance, wavelength) and very selective. VUV absorbance spectra are typically highly structured and distinct for individual compounds, yet often exhibit the intuitive property of having similar features within compound classes. Individual analyte speciation and bulk compound class characterization are both possible using GC-VUV.

VUV data is equally quantitative as it is qualitative. VUV spectral quantitation follows the simple linear relationship between absorbance and concentration described by the Beer-Lambert Law. VUV detection is mass-sensitive (1). The detector response is proportional to the amount of analyte present per unit time. An interesting feature of VUV spectroscopy is that if the VUV absorption cross-section for a chemical compound is known, the precise number of molecules in the detector can be determined based on the measured absorption signal. Typical instrument detection limits (IDLs) for analytes range from tens to low hundreds of picograms on column. Complete compound identification and quantitative analysis can be accomplished using a single VUV detector.

VGA Gas Chromatography Detectors

Measurement within the VUV spectrum has historically been restricted to bright source synchrotron facilities due to significant background absorption challenges inherent to the wavelength range. The VGA-100™ GC-VUV detector is the first bench-top spectrometer capable of full VUV spectrum detection (120 – 240 nm), and the VGA-101™ extends its wavelength detection range to 430 nm. Both detectors are compatible with most major GC manufacturers.

The detectors can be connected through a heated transfer line, which is inserted through a punch-out in the GC oven casing similar to a mass spectrometer. A makeup flow of carrier gas is introduced at the end of the transfer line. Analytes arrive in the flow cell and are exposed to VUV light from a deuterium lamp. Specially coated reflective optics paired with a back-thinned charged coupled device (CCD) enable the collection of high quality VUV absorption data. Figure 2 shows a schematic of the analyte path from GC to VUV detector.

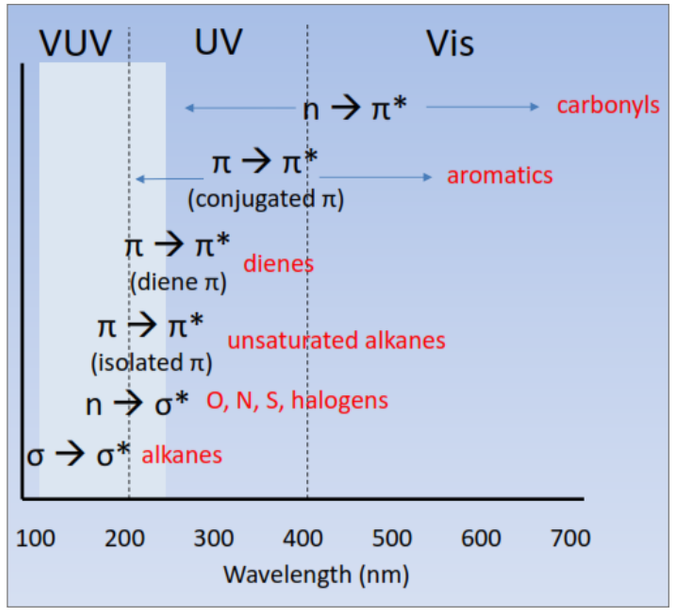

Figure 1: The electronic transitions probed by VUV light. σ→σ* and π→π* excited state transitions are captured by VUV detection and result in unique spectra for most compounds.

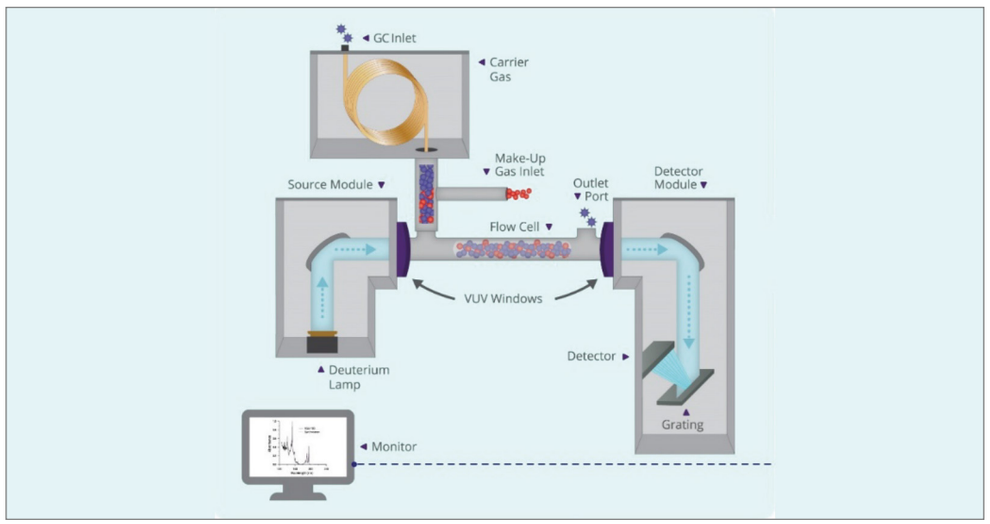

Figure 2: Schematic of the GC-VUV instrumental setup (not to scale). Dimensions of the detector are 30" x 13" x 17" or 76.2 x 33 x 43.2 cm. Flow cell volume is ~40 µL. Path length is 10 cm.

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The GC-VUV Toolkit

Differentiate Isomers

Most compounds have unique spectral profiles within the VUV wavelength range. Subtle differences in spectral features of isomeric analytes are recognized by VUV software and used to differentiate compounds that may only vary by functional group position. Goodness of fit information provided during post-run analysis helps to ensure that the correct VUV library compound has been matched with the analyte spectral response. The ability of GC-VUV to consistently discriminate between constitutional isomers complements mass spectrometry, which traditionally struggles in this respect.

Naphthols, xylenes, and cis- and trans-fatty acids are compounds that are prohibitively difficult to distinguish according to their electron ionization mass spectral profiles1. Xylenes present the additional challenge of natural co-elution that makes separating their isoforms problematic. Figure 3 shows the distinct VUV spectra of m-, p-, and o-xylene. These compounds can be differentiated despite their only difference being the position of two methyl groups around a benzene ring. As will be seen later, the spectral differences of these isomers enable their co-elution to be resolved through spectral deconvolution.

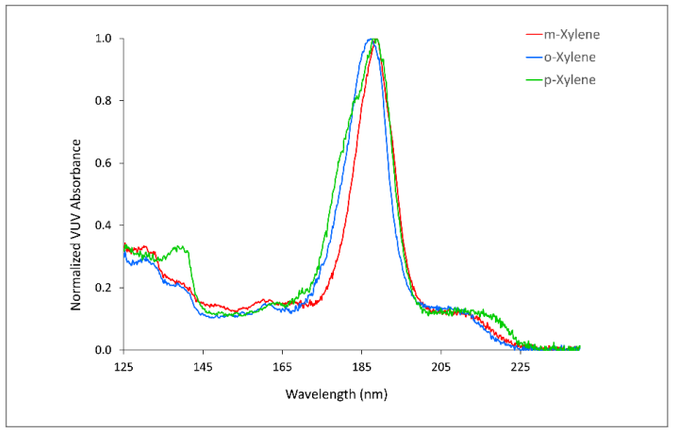


Figure 3: The distinct VUV spectra of m-, p-, and o-xylene. The compounds differ by only the positions of two methyl groups on a benzene ring, and are virtually impossible to distinguish by gas chromatography – mass spectrometry (GC-MS).

Fatty acid screening and profiling is an application that commonly requires the use of multiple detectors to achieve quantitative and qualitative results(2). FID is a quantitative detector that is suitable for routine screening when guided by retention index information. GC-MS has traditionally been used for qualitative compound profiling, but falls short where isobaric analytes are prevalent. It especially struggles with differentiating cis and trans fatty acid isomers. Electron impact ionization can also cause double bond migration and lead to ambiguous fatty acid structural data.

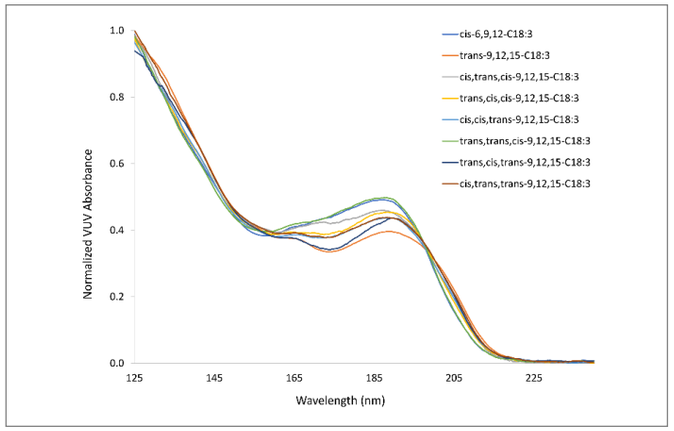


Figure 4: VUV spectra of fatty acid methyl ester (FAME) cis and trans isomers that are commonly found in butter and vegetable oils. GC-VUV can readily distinguish between the C18:3 FAME isomers, cis and trans classification, and the degree of unsaturation.

Determining cis and trans fatty acid distribution in oils and fats is important in assessing their potential health impacts. VUV spectra of trans-containing fatty acid methyl ester (FAME) isomers typically found in butter and vegetable oils are shown in Figure 4. These trans-containing isomers separate chromatographically from cis-containing isomers and have the tendency to co-elute with each other, and in some cases, with select C20:1 isomers. GC-VUV is not only able to differentiate the C18:3 FAME variants, but is also capable of telling cis isomers apart from trans isomers. Degrees of unsaturation such as C20:1 vs. C18:3 can additionally be distinguished. Previous work has demonstrated how distinct VUV spectra enable straightforward deconvolution and accurate quantitation of cis and trans FAME isomers1(3).

Fentanyl is a well characterized compound, but distinguishing between its isomeric forms such as valeryl fentanyl, parafluorofentanyl, and furanyl fentanyl can be problematic using traditional GC-MS methods. Figure 5 shows that when the VUV spectra of these isomers are overlaid, distinct differences are observed despite their structural similarity. Valeryl fentanyl varies only by the addition of two side chain carbon atoms and parafluorofentanyl by a fluorine atom attached to one of its benzene rings.

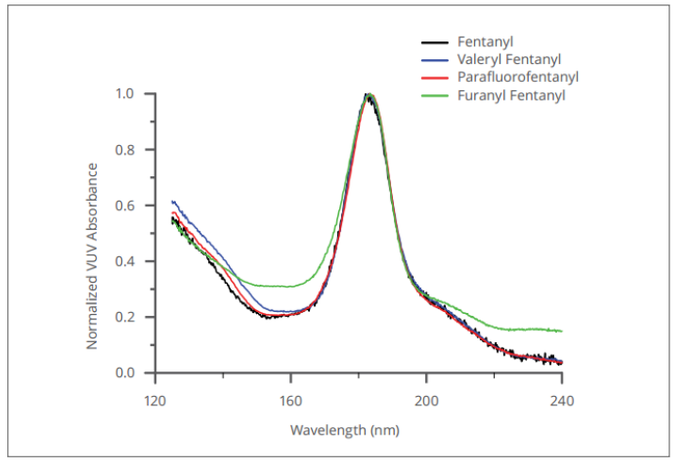


Figure 5: VUV spectral overlay of synthetic opioids fentanyl, parafluorofentanyl, valeryl fentanyl, and furanyl fentanyl.

Dimethylnaphthalene (DMN) isomers are substituted polycyclic aromatic hydrocarbons (PAHs) that are commonly found in crude oil and related products. These compounds vary in their different carcinogenicities, industrial uses, and environmental polluting effects and are typically difficult to differentiate even when chromatographic separation has been achieved. Figure 6 demonstrates the distinct spectral features of 1,4-dimethylnaphthalene, 2,3-dimethylnaphthalene, 1,3-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene that vary only by the position of two methyl groups. Schug, et al. used these unique VUV spectra to deconvolve mixtures of eight different DMN isomers (4).

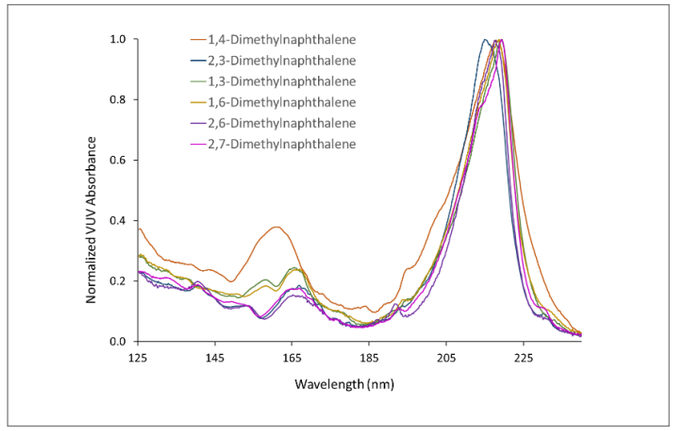


Figure 6: Normalized VUV spectra of dimethylnaphthalene isomers. These compounds have unique spectral features despite their structural similarity.

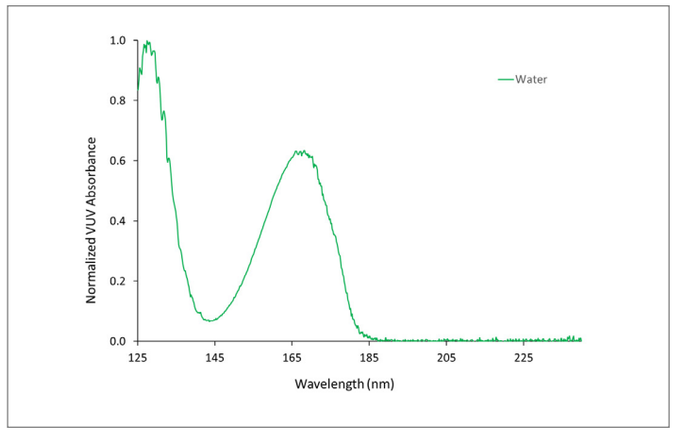
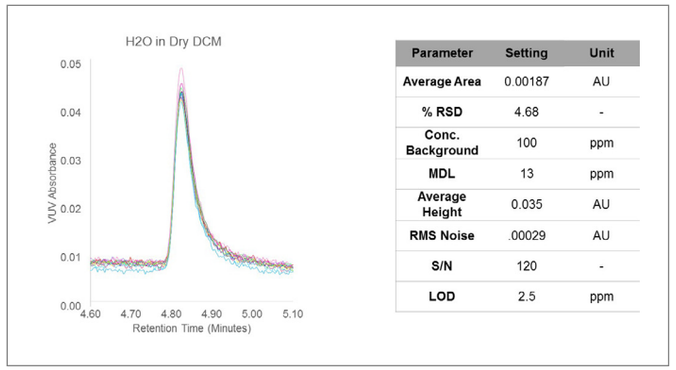


Figure 7: The normalized VUV spectrum of water.

Improve Analyte Selectivity

GC-VUV is selective for individual compounds due to their unique spectra. One example of selectivity that is unique to VUV spectroscopy is the ability to identify and quantitate water. The VUV spectrum of water can be seen in Figure 7. An initial study determined low ppm limits of detection with <5% RSD when water was determined in organic solvents (5). Example results are detailed in Figure 8. Jennerwein et al. separately demonstrated that quantitative analysis of water could be accomplished in fuel streams



Parameter	Setting	Unit
Average Area	0.00187	AU
% RSD	4.68	-
Conc. Background	100	ppm
MDL	13	ppm
Average Height	0.035	AU
RMS Noise	.00029	AU
S/N	120	-
LOD	2.5	ppm

Figure 8: Selected results of pilot study to determine water in organic solvents using GC-VUV. Low ppm detection limits with precision <5% RSD were observed.

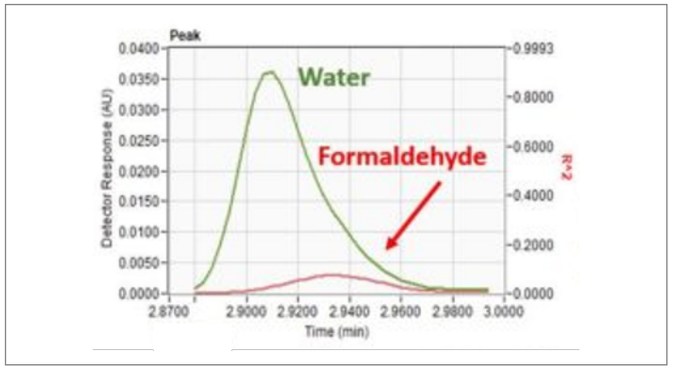


Figure 9: The VUV spectral deconvolution of water and formaldehyde in a Triethylene Glycol (TEG) sample. Formaldehyde was detected as a contaminant of TEG.

containing oxygenates without affecting their specification (6).

The capability of GC-VUV to selectively target most compounds enables analyses that previously required multiple detection methods to be performed on a single, universal VUV detector. GC-VUV methods have been developed for the determination of water in gasoline, ketone solvents, Triethylene Glycol (TEG), and other solvents. These methods simultaneously characterize other analytes within the respective sample matrices. A separate Karl Fischer titration step to quantify water is no longer needed when VUV spectroscopy is utilized. An example of VUV selectivity for individual compounds is shown in Figure 9. Small quantities of

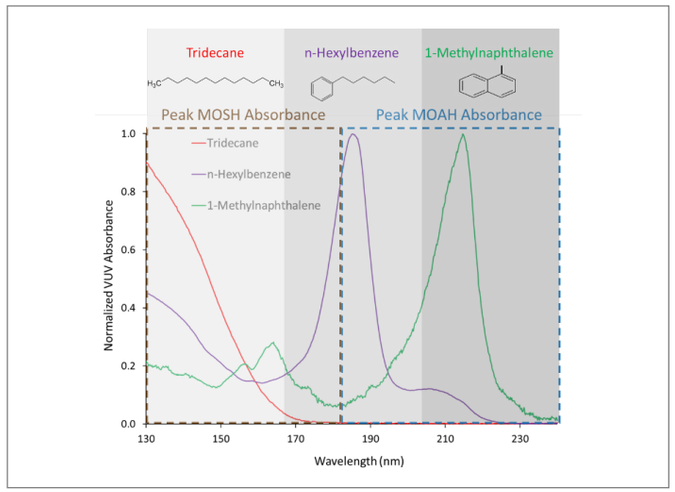


Figure 10: VUV spectral comparison of mineral oil saturated and aromatic hydrocarbons (MOSH and MOAH). The shading gradient demonstrates how spectral filters can be chosen during post-run data processing to selectively view absorption of different compound classes such as saturated, single-aromatic, and a multiple-ring aromatic compounds based on their absorbance maxima. The boxes show regions where MOSH and MOAH compounds have their peak absorbances, with 180 nm being a natural dividing line for selective spectral filters and the quantification of total compound area.

formaldehyde were detected co-eluting with water during a method run targeted for water and volatile petroleum hydrocarbons in TEG. Formaldehyde was identified as a contaminant of TEG while resolving the water peak co-elution through VUV deconvolution.

VUV spectral selectivity can be further exploited by applying spectral filters during post-run analysis to screen for compounds with similar absorption characteristics. This capability can be especially useful in applications where individual compound speciation is prohibitive. Compound classes can be selectively targeted and total area corresponding to their average response quantified.

Accurately differentiating between total saturated and aromatic hydrocarbons is an analytical challenge that is important in food safety, consumer product, and fuel refining applications. Determining the amount of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) is difficult due to the variety of hydrocarbons of different size and combinations of linear, branched, and cyclic structure. MOSH / MOAH determination has

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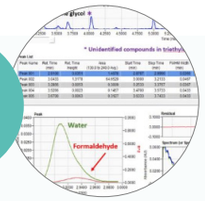

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traditionally been accomplished using LC-GC-FID methods that have long analysis times. H.-G. Janssen, et al. demonstrated that MOSH and MOAH can be analyzed in food products using a 25-minute GC-VUV method that uses direct injection (7).

MOSH and MOAH compounds can be selectively targeted because they absorb in different regions of the VUV spectrum. Figure 10 provides a VUV spectral comparison of a saturated, single-aromatic, and a multiple-ring aromatic compound. It is clear from the wavelength regions where these species have their peak absorbances that the selective use of spectral filters can target each class of compounds. Furthermore, the difference between the wavelength ranges where saturated and aromatic hydrocarbons absorb is apparent when 180 nm is used as a dividing line between the compound classes. These differential absorbance characteristics enable selectively targeting MOSH and MOAH for total area quantification.

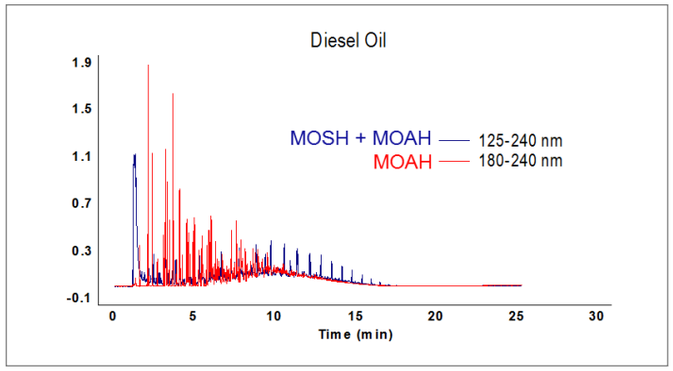

Figure 11: GC-VUV chromatogram of a diesel oil sample with high aromatic hydrocarbon content. Spectral filters of 120 – 240 nm (total MOSH and MOAH) and 180 – 240 nm (MOAH) have been applied during post-run processing to selectively view the relative amounts of saturated and aromatic hydrocarbons.

Aromatic hydrocarbons in raw materials can be measured with detection limits ranging from 0.2 to 2% depending on sample complexity. Figure 11 shows an example of high aromatic hydrocarbon content in diesel oil. The spectral filter of 180 – 240 nm is selective for aromatics, and its proportion relative to the saturated hydrocarbons is apparent. Figure 12 contrasts the diesel example with a mineral oil sample that has low aromatic hydrocarbon and high saturated hydrocarbon compound concentrations.

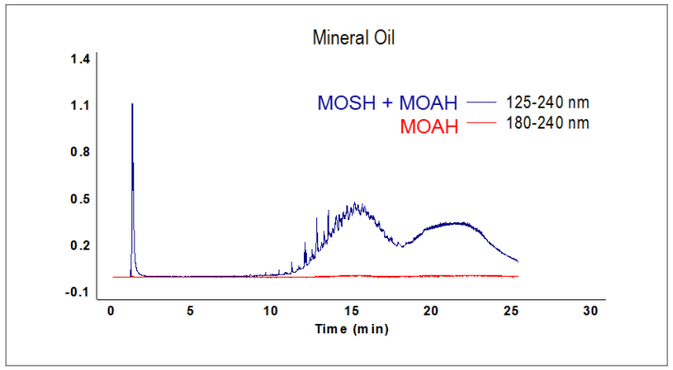

Figure 12: GC-VUV chromatogram of a mineral oil sample with low aromatic and high saturated hydrocarbon content. Spectral filters of 120 – 240 nm (total MOSH and MOAH) and 180 – 240 nm (MOAH) have been applied during post-run processing to selectively view the relative amounts of saturated and aromatic hydrocarbons.

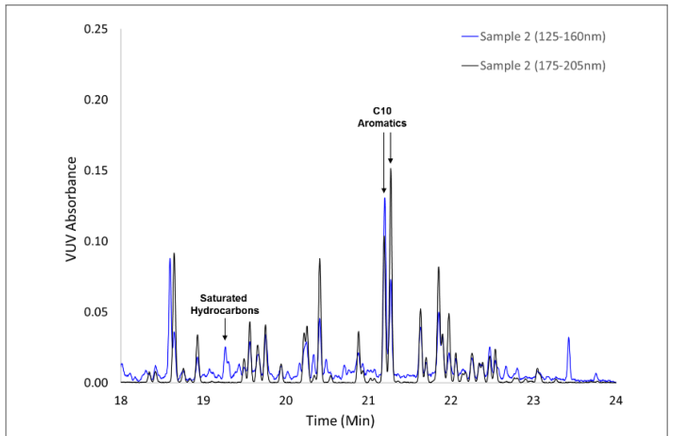

Figure 13: GC-VUV chromatogram of blended gasoline sample containing significant co-elution of saturated hydrocarbons with C10-C12 aromatics (~C10 aromatics region shown). Spectral filters have been applied during post-run data analysis to highlight the relative amounts of aromatics (175-205nm) and saturates (125-160nm) present in the sample. The comparison shows significant saturate response between and overlapping with the aromatic peaks. GC-VUV eliminates the error of over-reporting aromatics and under-reporting saturates by using spectral response differences to provide accurate total area quantitation of each compound class.

Accurately determining the amount of aromatic and saturated hydrocarbons in gasoline is also challenging using methods based on GC-FID. This is especially true when samples contain high concentrations of both compound classes. Using a detector capable of reporting only response and retention time often results in over-estimating aromatic concentration and under-estimating saturated hydrocarbon content. GC-VUV eliminates this error by using spectral response differences to provide accurate total area quantitation of each compound class. The potential for compound misidentification is apparent in Figure 13 where spectral filters have been applied during post-run analysis to a blended gasoline sample with high concentrations of saturated and aromatic hydrocarbons. The ability to differentiate the compounds by their absorbance responses enables VUV software to provide accurate characterization of their relative amounts. The GC-VUV chromatogram in Figure 14 demonstrates how saturated and aromatic hydrocarbons are easily deconvolved by VUV Analyze™ software. As will be discussed later, the data processing software uses proprietary algorithms to provide this type of automated analysis.

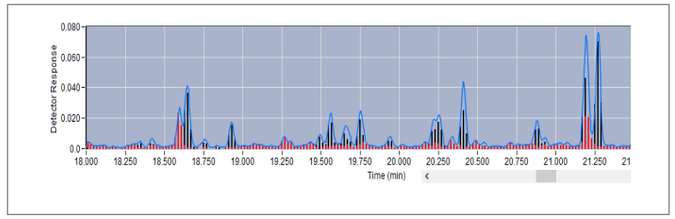

Figure 14: Deconvolved GC-VUV chromatogram of the blended gasoline sample containing high C10-C12 saturated hydrocarbon and aromatic content. VUV AnalyzeTM software performs automated deconvolution of the co-eluting saturates and aromatics.

Differences in compound absorbance profiles can also be exploited within a class. The spectral filter comparison in Figure 15 shows the relative proportion of monoaromatics, diaromatics, tri-aromatics, and multiple ring aromatic species in a diesel fuel fraction. Other sub-categories that have been selectively targeted for compound class analysis include non-conjugated diolefins, conjugated diolefins, cycloolefins, and conjugated hexadienes.

Deconvolve Co-Eluting Peaks

Unique VUV absorbance spectra not only enable unambiguous

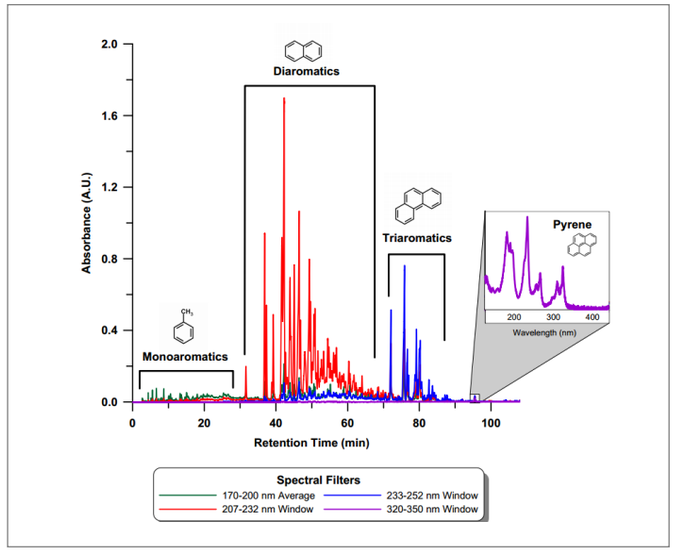

Figure 15: Spectral filter comparison of diesel fuel fraction analyzed from 120 – 350nm. Total area for monoaromatics, diaromatics, tri-aromatics, and multiple ring aromatics can be determined by selecting the wavelength region where their absorbance is most intense.

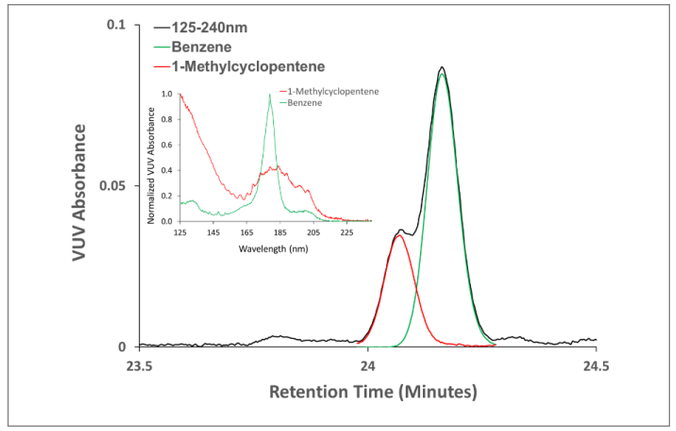

Figure 16: GC-VUV chromatogram of gasoline sample zoomed-in to show the co-elution of benzene and 1-methylcyclopentene. A chromatographic shoulder starting at 24 minutes is observed from the full range absorbance (125 – 240 nm) response. The deconvolution performed by VUV software during post-run analysis is overlaid to display the relative proportion of both compounds. The VUV Absorbance spectra of benzene and 1-methylcyclopentene are displayed in the figure inset to demonstrate how their unique spectral profiles enable straightforward identification and deconvolution.

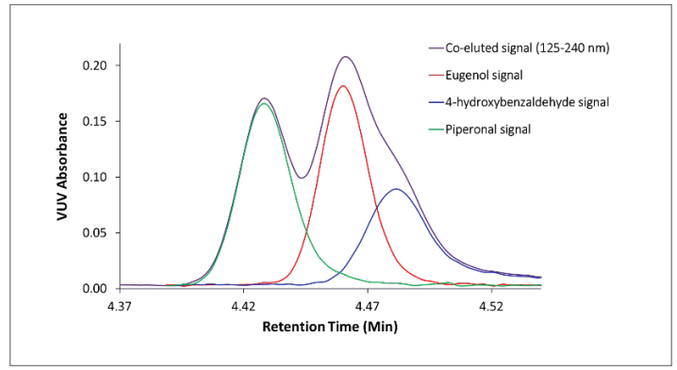

Figure 17: The co-elution of piperonal, eugenol, and 4-hydroxybenzaldehyde that resulted from a 6-minute GC-VUV method used to screen natural and artificial flavoring compounds. The reconstructed peak overlay shows their relative proportion under the co-eluted peak.

compound identification, but also enable co-eluting analytes to be resolved by VUV spectral deconvolution. VUV absorption is additive, meaning that overlapping peaks give a spectrum that corresponds to the sum absorbance of each compound. The individual contribution of each analyte can be determined if the VUV spectra for co-eluting compounds are stored in the VUV library (8).

This feature of GC-VUV is particularly useful for resolving compounds that naturally co-elute. The co-elution of benzene and 1-methylcyclopentene can be seen in the GC-VUV chromatogram in Figure 16. These compounds commonly co-elute in gasoline samples and require significant effort to resolve chromatographically. A reconstructed chromatogram is overlaid to display the relative proportion of benzene and 1-methylcyclopentene following the deconvolution of their VUV absorbances. The VUV Absorbance spectra of both compounds are displayed in the figure inset to demonstrate how their unique spectral profiles facilitated the straightforward resolution of their overlapping peaks.

VUV deconvolution capabilities can also be applied in instances where multiple analytes co-elute. Figure 17 shows the co-elution of piperonal, eugenol, and 4-hydroxybenzaldehyde that resulted when a 6-minute GC-VUV method was used to analyze a mixture of 10 natural and artificial flavoring compounds (9). It is apparent from the reconstructed peak overlay that the only way to have accurately quantitated their relative proportion was through VUV spectral deconvolution.

Schug and co-workers defined practical operating limits of VUV deconvolution based on the degree of spectral similarity and relative abundance4. Compounds with dissimilar spectra can be reliably deconvolved when their relative abundances are within three orders of magnitude. Analytes with similar spectra can be deconvolved when concentration differences are within two orders of magnitude. The latter limitation was demonstrated with dimethylnaphthalene (DMN) isomer concentration ratios that varied by as much as 99:1 (specifically, 990 ppm: 10 ppm). The degree of spectral similarity of these DMN isomers can be seen in Figure 6.

Reduce GC Run Times

The ability to readily resolve co-elution through VUV spectral deconvolution enables GC run times to be deliberately shortened. VUV detectors operate at ambient pressure and are thus not flow rate limited. Chromatography can be compressed by increasing the GC column flow and oven temperature program rates.

Testing for the presence of residual solvents in Active Pharmaceutical Ingredients (APIs) is critical for patient safety and commonly follows United States Pharmacopeia (USP) Method <467> guidelines, or more broadly, International Council for Harmonization (ICH) Guideline Q3C(R6). The gas chromatography (GC) runtime suggested by USP Method 467 is approximately 60 min.

A generic method for residual solvent analysis by GC-MS describes conditions that include a runtime of approximately 30 minutes (10). A GC-VUV and static headspace method was developed using a chromatographic compression strategy that resulted in a GC runtime of 8 minutes. The GC-VUV method uses a flow rate of 4 mL/min and an oven ramp of 35°C (held for 1 min), followed by an increase to 245°C at a rate of 30°C/min.

Figure 18 compares the results when GC-MS method conditions were applied to GC-VUV instrumentation against the GC run and elution times when fast GC-VUV method conditions were used to analyze Class 2 residual solvents on the same setup. Tetralin eluted at approximately 35 minutes using the GC-MS method conditions, whereas the analyte had a retention time of less than 7 minutes when the fast GC-VUV method was applied. The co-elution of m- and p-xylene occurred in both GC-MS and GC-VUV method runs.

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New Method for Residual Solvent Characterization by GC-VUV

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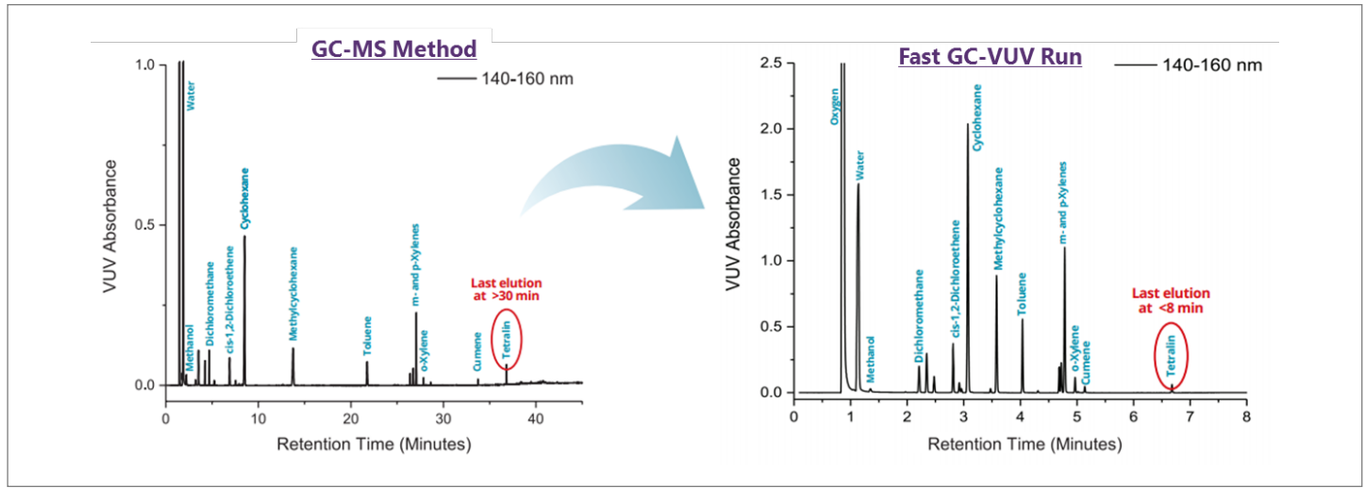


Figure 18: Comparison of runtimes when legacy GC-MS and fast GC–VUV method conditions were used for residual solvent analysis. Tetralin elutes at >30 minutes using the GC-MS method conditions on GC-VUV instrumentation. In contrast, tetralin elutes at <7 minutes when fast GC-VUV method conditions are applied.

VUV software matched the analyte absorbance of both isomers with VUV library spectra (Figure 3) to deconvolve the overlapping signals as displayed in Figure 19. Goodness of fit information confirms that the correct compound assignment takes place during the post-run data analysis.

The flow rate-enhanced chromatographic compression strategy has also been used to shorten the GC run times associated with terpene analysis. Terpene characterization has traditionally been performed through a combination of gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS). Baseline resolution of analyte peaks is often needed for accurate quantification by either technique due to the isomeric nature of many terpenes. The burden of complete separation can lead to relatively long GC run times. Because GC–VUV is able to spectrally distinguish isomers and quantitatively deconvolve co-eluting peaks, these run times can be significantly reduced.

Separation times for terpene analysis using GC–FID or GC–MS can take 30 min or more. The GC–VUV method developed for 21 terpene standards reduced the GC run time to approximately 10 min, with the last analyte eluting before 9 min (Figure 20). Several co-elutions were observed for the early-eluting monoterpenes, including β-pinene and β-myrcene, α-terpinene and cis-ocimene,

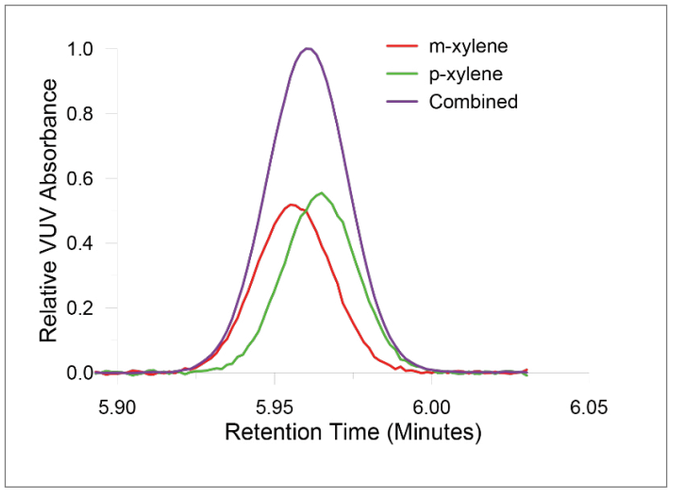


Figure 19: The deconvolution of m- and p-xylene co-elution. The relative contribution of each analyte is shown relative to the sum absorbance.

and between limonene, p-cymene, and trans-ocimene.

Even though these monoterpenes are structural isomers (with the exception of monoterpenoid p-cymene), they all produce unique absorbance spectra (Figure 21). Because VUV absorbance

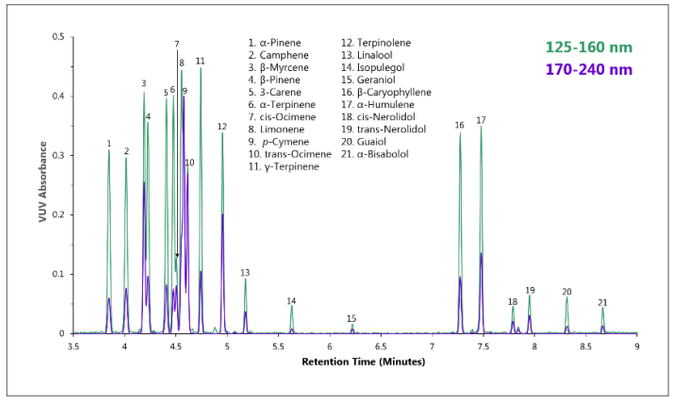


Figure 20: Chromatogram of a terpenes standard mix (two spectral filters shown for visualization purposes). The last terpene compound elutes before 9 min.

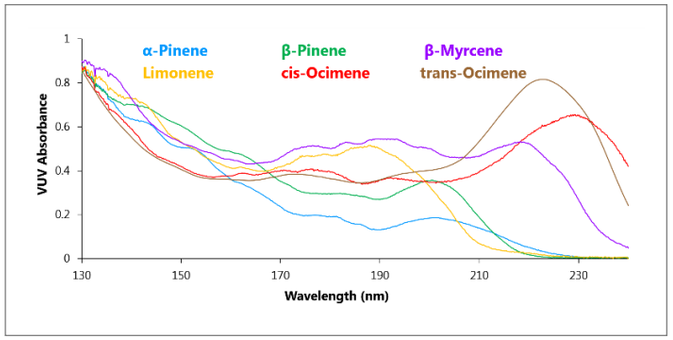


Figure 21: Absorbance spectra of 6 monoterpene isomers. Though some similarities exist between closely related compounds (e.g., α- and β-pinene, cis- and trans-ocimene), each spectrum is still easily distinguished.

is directly proportional to the concentration of analyte passing through the flow cell, these unique absorbance spectra can be used to deconvolve co-eluting peaks accurately.

Figure 22 provides an example of how deconvolution is performed for limonene and p-cymene using their spectral responses. The individual spectra of the terpenes are shown in Panel A along with the summed absorbance of the selected retention time window (blue region in Panel B) and the spectral fit with VUV library reference spectra. The R2 >0.999 fit result confirms the correct compound identification by the VUV library and enables the subsequent deconvolution performed by VUV software.

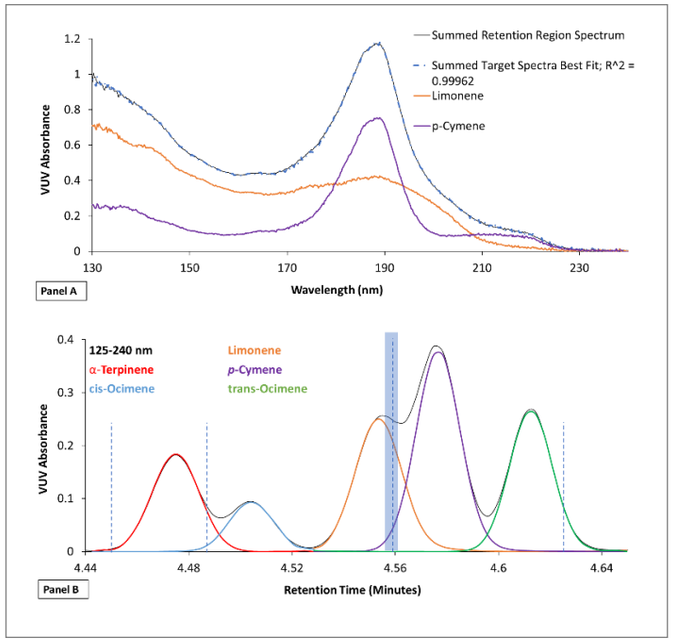


Figure 22: Panel A shows the individual spectra of limonene and p-Cymene along with the summed absorbance of the selected retention time (blue region in Panel B) and the fit with VUV library spectra. The deconvolution of these and other terpenes analyzed by fast GC-VUV is featured in Panel B.

Additional work has been done using the capabilities of GC-VUV to characterize terpenes and turpines (11).

It has also been shown that GC runtimes for hydrocarbon analysis in gasoline can be shortened dramatically using GC-VUV methods. Typical GC separation times for determining the total amount of paraffin, isoparaffin, olefin, naphthene, and aromatic (PIONA) hydrocarbons in gasoline range samples vary between 1 – 3 hours using legacy methods. ASTM D8071 (described later in this text) reduces the GC run and analysis time to approximately 34 minutes. Method translation experiments conducted after the method's approval have demonstrated that GC run times as short as 14 minutes can be used to determine total PIONA content in gasoline samples. VUV Analyze™ software enables this faster GC-VUV approach by deconvolving analyte co-elution during its automated data processing routine.

Automate Data Processing

Speciating analytes in complex mixtures in order to understand the relative proportion of compounds that are critical to production can be both labor-intensive and error-prone when methods that rely on retention time and detector response are utilized. Separating compounds in order to achieve high confidence in peak assignment often involves the use of long columns and run times. Peak identification requires a combination of calibration procedures, matching observed peaks against known chromatographic profiles, and data processing oversight.

VUV spectra are similar within compound classes and can be used to determine the relative group composition within a sample. Because of this shared spectral similarity, VUV Analyze™ data processing software is able to apply fitting procedures to quickly determine the relative contribution of each compound category present. The automated data analysis package implements equations and fit algorithms that utilize time interval deconvolution (TID) to divide a chromatogram into equal, small time intervals (typically <0.05 min)(12). For each time interval the measured spectrum is compared against reference spectra in the designated VUV library, and the best analyte(s) fit is determined. The software quickly measures the total response per analyte for a given chromatogram during its data processing procedure.

This automated data processing requires the user to simply locate a run file and then initialize the analysis once the initial setup has been completed. Retention index information is used to limit the amount of VUV library searching and fitting performed for each analyte, enabling fast data processing times. Compound class and specific compound concentrations are reported in either mass or volume percent. No manual peak assignment is required, and reports are typically generated in less than 1 minute per sample.

GC-VUV bulk compound characterization was first applied to the analysis of paraffin, iso-paraffin, olefin, naphthene, and aromatic (PIONA) hydrocarbons in gasoline streams. The associated method ASTM D8071 eliminates the need for multiple column use and complex instrumental setup while providing a total analysis time 34 minutes per sample. A typical VUV Analyze™ chromatographic analysis is displayed in Figure 23. The inset shows how the analyte spectral response is fit with VUV library spectra for the selected time slice. VUV Analyze™ provides a report detailing the carbon number breakdown within each PIONA compound class, as well as the relative mass or volume percent of classes within the sample. A

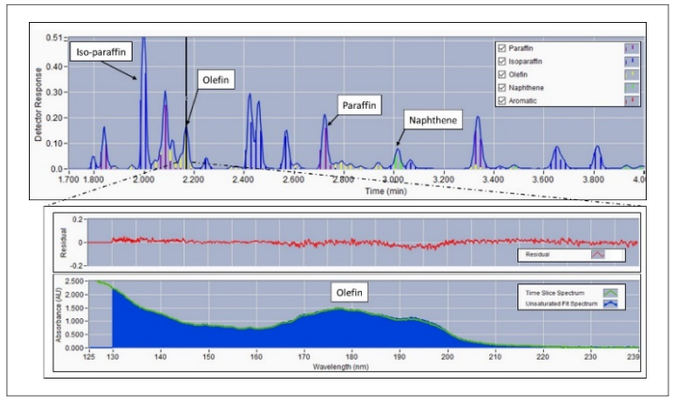
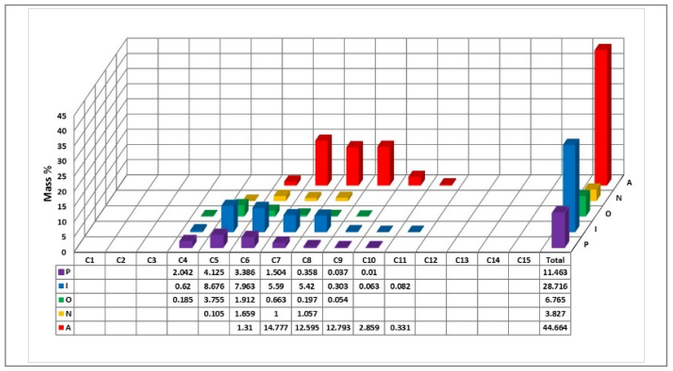


Figure 23: Zoomed-in chromatogram of gasoline sample with key PIONA compound class representative peaks labeled. Inset figure shows analyte spectral features fit with VUV library olefin compound class spectral response information. The residual fit statistical data indicating a good fit is also shown.



	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	Total
P				2.042	4.125	3.386	1.504	0.358	0.037	0.01						11.463
I				0.62	8.676	7.963	5.59	5.42	0.303	0.063	0.082					28.716
O				0.185	3.755	1.912	0.663	0.197	0.054							6.765
N					0.105	1.659	1	1.057								3.827
A						1.31	14.777	12.595	12.793	2.859	0.331					44.664

Figure 24: Compositional analysis of gasoline sample run using ASTM D8071. Carbon number and mass % or volume % composition of PIONA compounds are reported by VUV Analyze™ automated software.

table with mass % and carbon number data from a gasoline sample run using ASTM D8071 can be seen in Figure 24.

Compositional analysis using VUV Analyze™ has also been applied to the characterization of terpenes. A standard mixture of terpenes was analyzed by liquid 1-µL injections. Figure 25 displays two different time ranges of the resulting GC-VUV run as viewed in the VUV Analyze™ chromatogram window. The vertical bar shading represents the relative proportion of each terpene in the

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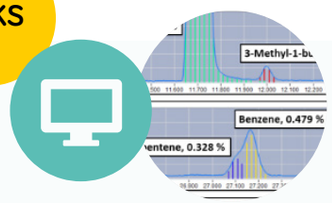

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PIONA GC analysis addressing the complexities of fuels

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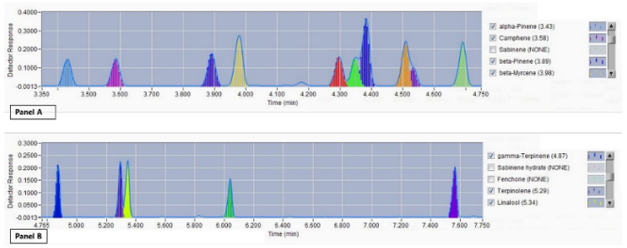

Figure 25: GC-VUV chromatogram of a standard terpene mixture. The deconvolution of 3-carene (red), α-terpinene (green), p-cymene (blue), limonene (orange), and cis-ocimene (purple) can be seen in the VUV Analyze™ chromatogram window displayed in Panel A, the resolved co-elution of terpinolene and linalool can be observed in Panel B.

Terpenes Standard Mixture			
Analyte	Mass %	Analyte	Mass %
α-Pinene	5.15	Isopulegol	4.73
Terpinolene	5.03	Linalool	4.72
β-Pinene	5.01	Geraniol	4.67
γ-Terpinene	4.91	cis-Ocimene	4.66
Camphene	4.90	β-Caryophyllene	4.65
cis-Nerolidol	4.83	α-Humulene	4.65
Limonene	4.83	β-Myrcene	4.64
3-Carene	4.83	trans-Nerolidol	4.58
p-Cymene	4.79	α-Bisabolol	4.53
α-Terpinene	4.77	Guaiol	4.37
trans-Ocimene	4.75		

Table 1: Quantitative GC-VUV analysis of standard terpene mixture using VUV Analyze™ compositional analysis. Values are given in relative mass %, but relative volume % and absolute concentration can be determined by applying density and external calibration curve information, respectively.

Eucalyptus Essential Oil			
Analyte	Mass %	Analyte	Mass %
Eucalyptol	68.46	β-Pinene	0.62
α-Terpineol	12.66	Sabinene	0.59
Limonene	4.71	Geraniol	0.58
4-Terpineol	2.69	Linalool	0.37
α-Pinene	2.49	α-Terpinene	0.31
cis-Ocimene	1.37	Terpinolene	0.17
β-Myrcene	1.28	trans-Citral	0.16
α-Phellandrene	1.05	β-Caryophyllene	0.12
trans-Ocimene	0.85	cis-Citral	0.06
p-Cymene	0.80	Nerol	0.03
γ-Terpinene	0.62		

Table 2: Quantitative GC-VUV analysis of eucalyptus essential oil using VUV Analyze™ compositional data analysis.

Neroli Essential Oil	
Analyte	Mass %
Linalool	51.68
Linalyl acetate	8.34
Limonene	7.46
α-Terpineol	7.09
β-Pinene	6.82
trans-Ocimene	4.27
Geraniol	3.63
Geranyl acetate	2.74
trans-Citral	2.25
Nerol	1.98
cis-Ocimene	1.95
trans-Nerolidol	1.51
β-Caryophyllene	0.28

Table 3: Quantitative GC-VUV analysis of neroli oil using VUV Analyze™ compositional data analysis. Small percentages of nerol and trans-nerolidol were detected as a result of liquid injection, demonstrating the difficulty in partitioning these compounds into headspace in the presence of a water matrix.

sample. The deconvolution of 3-carene, α-terpinene, p-cymene, limonene, and cis-ocimene can be seen in Panel A, and the resolved co-elution of terpinolene and linalool can be observed in Panel B. The quantitative analysis of the standard mixture is shown in Table 1.

The same methodology was applied to the characterization of essential oils. Table 2 displays the quantitative analysis of eucalyptus. Table 3 contains the results of neroli oil analysis. Small quantities of nerol and trans-nerolidol were detected using the liquid injection strategy. These compounds did not appear to be amenable to headspace partitioning from the water matrix used in the experiment, and may have been under-reported. That said, the relative masses of nerol and trans-nerolidol were still lower than expected relative to literature values.

Compositional analysis using time interval deconvolution automated by VUV Analyze™ has also been used to determine the chlorine content in Aroclor mixtures (13). The chlorine percentages reported were in good agreement with their stated nominal values, suggesting that the GC-VUV TID procedure could be utilized to rapidly speciate and classify polychlorinated biphenyls (PCBs) in Aroclor mixtures. VUV Analyze™ can be customized to automate the characterization of a wide variety of analytes and compound classes, thus speeding up the time to data and improving reporting accuracy where relative % analysis is appropriate.

Develop Scalable Methods

The straightforward nature of VUV spectral data eliminates guesswork related to retention time-based identification and makes the technology accessible to users in both R&D and production settings. GC-VUV is well suited for use in production environments where relative compositional analysis is desired. The ability to use VUV spectroscopy to generate robust data sets from a scalable method was recognized by ASTM International when it approved "Standard Test Method for the Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds

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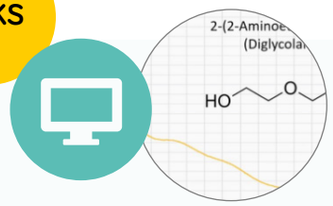

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Overview of PIONA GC analysis simplified by VUV Analyze™ software

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EPA Referee Method	Parameter	VUV QC Gasoline Avg (47 runs)	Reproducibility (R) of Referee Method	EPA Max Allowable SD (0.3*R)	D8071 VUV SD (n=47)
ASTM D5599	Oxygen, mass%	3.64	0.38	0.11	0.03
ASTM D1319	Olefins, vol%	14.4	4.1	1.23	0.21
ASTM D1319	Aromatics, vol%	21.9	3.7	1.1	0.3
ASTM D3606	Benzene, vol%	0.358	0.096	0.029	0.003

Table 4: Site precision study results of D8071 using EPA 40 CFR 80.47 guidelines for measuring fuel parameters. Oxygen, aromatic, olefin and benzene standard deviations (SD) from forty-seven D8071 runs were all within the required maximum allowable SD specified by EPA, and typically 4 – 10X better than required.

in Automotive Spark-Ignition Engine Fuel using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)" as D8071 for the analysis finished gasoline. The parameters of this method have subsequently been used with the VUV PIONA+™ product solution to characterize relative PIONA concentrations of other fuel streams including reformate, reformer feed, FCC, light naphtha, and heavy naphtha samples.

The VUV PIONA+™ product solution includes a VGA-100 GC detector, VUV Analyze™ automated data processing software configured for PIONA compositional analysis, and a gasoline component VUV spectral library.

The robustness of ASTM D8071 was demonstrated through an exploratory site precision study that was performed at VUV Analytics headquarters. Initial results indicated that the method shows exceptional precision relative to EPA referee methods when judged by the agency's 20/20 rule. D8071 is capable of superior precision as compared to separate referee EPA methods (D1319, D3606 and D5599) for typical gasoline compositional analysis parameters.

EPA precision criteria were applied to forty-seven commercial gasoline sample runs using ASTM D8071 with a VGA-100 detector over a period ranging from Jan 3 – Jan 23, 2018. No single result was omitted or defined as an outlier, and results were recorded and statistically compared to the EPA precision criteria. Table 4 shows that oxygen, aromatic, olefin and benzene standard deviations (SD) from forty-seven D8071 runs were all within the required maximum allowable SD specified by EPA, and typically 4 – 10X better than required.

The flexibility to tailor the analytes speciated by VUV Analyze™, as well as the compound classes and subcategories characterized, to meet changing quality control requirements further demonstrates the suitability of GC-VUV for production environments. A method known as VUV Verified™ Hydrocarbon Analysis (VUV-VHA™) utilizes retention time, retention index, and spectral information to speciate approximately 140 compounds commonly found in gasoline, while fully characterizing PIONA group composition of samples. VUV Analyze™ setup for VUV-VHA™ analysis requires an initial setup step of checking compound retention times from the user's chromatography system against database information supplied by VUV Analytics, then making retention time window adjustments where necessary. Once initial GC runs with its parameters have been completed, the user simply loads the relevant run files and initiates the VUV Analyze™ data processing procedure. Figure 26 provides an example VUV Analyze™ report output of a gasoline analysis using the VUV-VHA™ method.

VUV Analyze™ is setup for relative PIONA compound compositional analysis, but can also be customized to include sub-categories of interest. This capability has been used to determine non-conjugated diolefins, conjugated diolefins, cycloolefins, conjugated hexadienes, and di-aromatics. An example of olefin subclass analysis is shown in Figure 27. A chromatographic time slice resulting from an ASTM D8071 method run is deconvolved in the VUV Analyze™ analysis window. A total olefin concentration of 37% was reported that included 0.2% non-conjugated diolefins, 0.3% conjugated diolefins, 4.5% cycloolefins, and 0.1% conjugated hexadienes. Olefins that did not belong to these sub-categories, such as trans-2-heptene, were accounted for in the remaining 31.9% reported as total olefin %.

The scalability of GC-VUV methods and flexibility of VUV

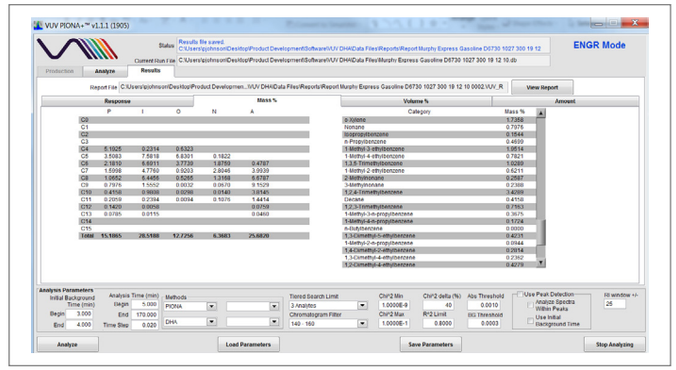

Figure 26: A snapshot of VUV-VHA™ reporting. The speciation of approximately 140 gasoline analytes and PIONA compound class analysis is automated and reported in both mass and volume% by VUV Analyze™ software. The total data analysis time per sample is between 2 – 3 minutes.

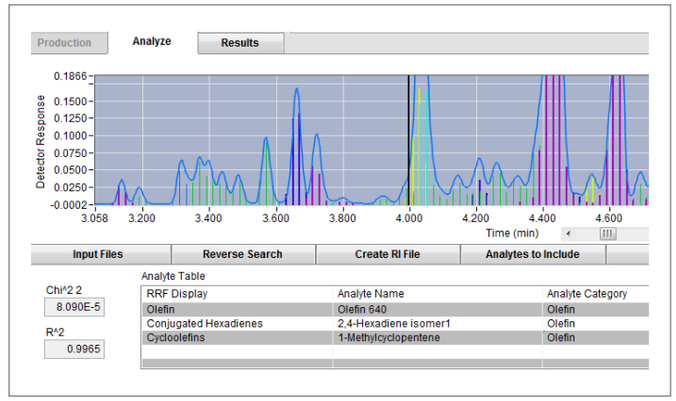

Figure 27: A time slice in the VUV Analyze™ post-run analysis window that highlights the deconvolution of an olefin, conjugated hexadiene, and cycloolefin. VUV Analyze™ reports olefin subcategories along with total olefin mass %.

Analyze™ software provide a total solution to production environments constrained by analysis time and the availability of skilled personnel. VUV Analyze™ Production Mode also removes any guesswork involved in analysis parameter adjustments by limiting end users to the steps of locating run files and initiating data processing in order to receive a report. The combined effect of GC-VUV capabilities and production-ready software is faster time to data with reduced reporting error.

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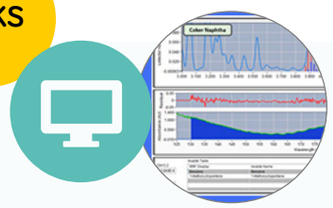

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VUV PIONA+ extends its compound class capabilities in fuel stream analysis

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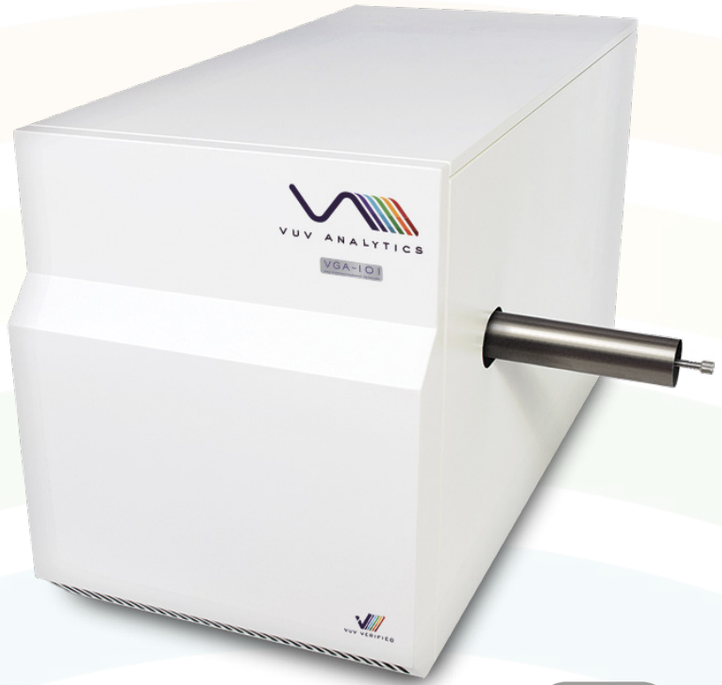
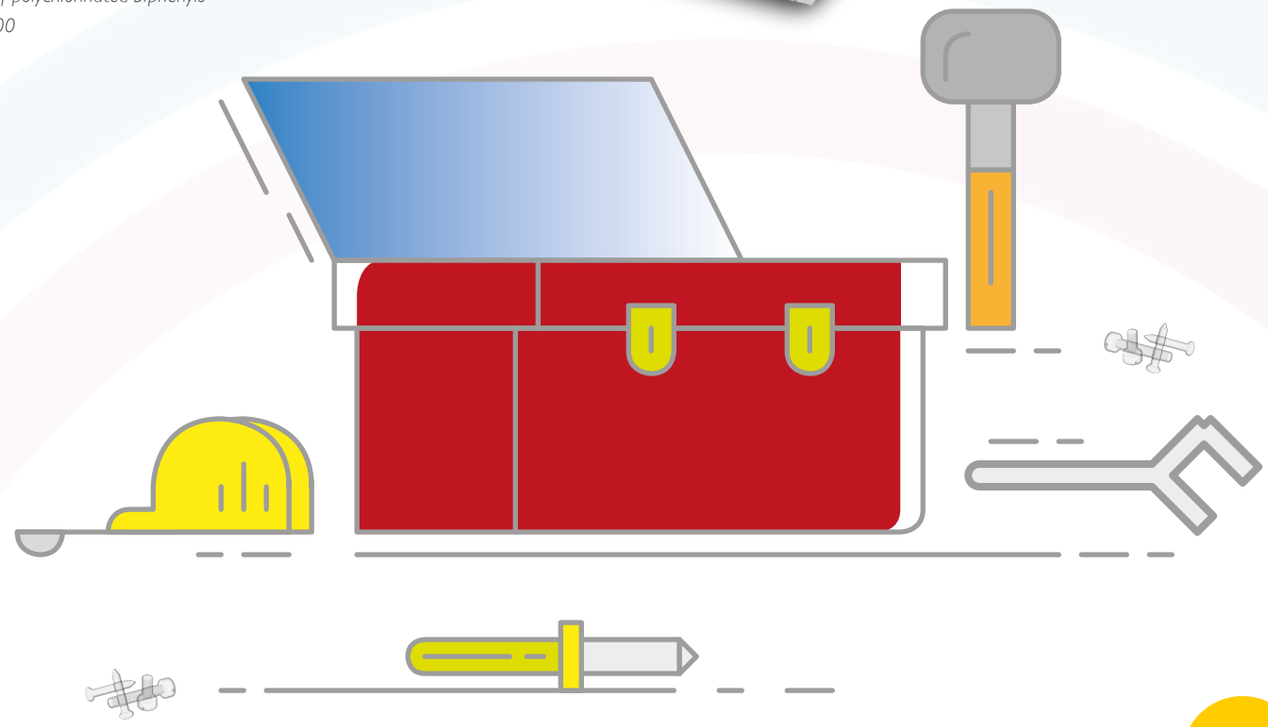
Conclusion

VUV spectroscopy has unique features that address many of the challenges inherent to gas chromatographic separation and detection. VUV light probes electronic transitions that are unique to individual compound structure. VUV spectral fingerprints are used to differentiate closely related compounds, including structural isomers. GC-VUV provides unique selectivity for individual compounds like water, as well as compound classes that are prohibitively difficult to speciate. VUV deconvolution capabilities can be used to resolve both isomer and multiple analyte co-elution, while also enabling GC runtimes to be significantly reduced through flow rate enhanced chromatographic compression. VUV Analyze™ can be customized to provide automated compositional analysis of a wide variety of analytes and compound classes. The GC-VUV toolkit helps to solve common GC challenges by providing capabilities that result in faster time to data with reduced reporting error.

References

1. *K.A. Schug, I. Sawicki, D.D. Carlton, H. Fan, H.M. McNair, J.P. Nimmo, P. Kroll, J. Smuts, P. Walsh, D. Harrison, Vacuum ultraviolet detector for gas chromatography, Anal. Chem. 2014, 86, 8329–8335*
2. *H. Fan, J. Smuts, L. Bai, P. Walsh, D.W. Armstrong, K.A. Schug, Gas chromatography–vacuum ultraviolet spectroscopy for analysis of fatty acid methyl esters, Food Chem. 2016, 194, 265–271*
3. *C. Weatherly, Y. Zhang, J. Smuts, H. Fan, C. Xu, K.A. Schug, J.C. Lang, D.W. Armstrong, Analysis of Long-Chain Unsaturated Fatty Acids by Ionic Liquid Gas Chromatography, J. Agric. Food Chem. 2016, 64, 1422–1432*
4. *J. Schenk, J. X. Mao, J. Smuts, P. Walsh, P. Kroll, K.A. Schug, Analysis and deconvolution of dimethylnaphthalene isomers using gas chromatography vacuum ultraviolet spectroscopy and theoretical computations, Anal Chim Acta, 2016, 945, 1-8*
5. *L. Shear-Laude, GC–VUV Absorbance Spectroscopy for the Quantitative Determination of Trace and Bulk Water in Organic Solvents, The Column, 2017, 13 (2), 9-13*
6. *M. Jennerwein, U. Käfer, M. Sarji, D. Harrison, J. Wendt, T. Wilharm, R. Zimmermann, T. Gröger, State-of-the-art Analytical Techniques for a Changing Feed- and Products Landscape in Petrochemistry, DGMK International Conference 2017.*
7. *H.-G. Janssen, R. Biersteker, A. G. Cicourel, Hyphenated LC-GC and Comprehensive LC×GC with VUV Detection for the Analysis of Aromatic Hydrocarbons in Food Products, RAFA Conference 2017.*
8. *K.A. Schug, I.C. Santos, Recent advances and applications of gas chromatography vacuum ultraviolet spectroscopy, J. Sep. Sci. 2017, 40, 138–151*
9. *K.A. Schug, I.C. Santos, J. Smuts, Rapid Profiling and Authentication of Vanilla Extracts Using Gas Chromatography-Vacuum Ultraviolet Spectroscopy, Food Anal. Method. 2017, 10 (12), 4068–4078*
10. *A Generic Method for the Analysis of Residual Solvents in Pharmaceuticals Using Static Headspace-GC-FID / MS, Application Note 5989-9726EN, Agilent*
11. *K.A. Schug, C. Qiu, J. Smuts, Analysis of terpenes and turpentines using gas chromatography with vacuum ultraviolet detection, J Sep Sci. 2016, 40 (4), 869-877*
12. *P. Walsh, M.Garbalena, K.A. Schug, Rapid analysis and time interval deconvolution for comprehensive fuel compound group classification and speciation using gas chromatography – vacuum ultraviolet spectroscopy, Anal. Chem. 2016, 88 (22), 11130–11138.*
13. *C. Qiu, J. Cochran, J. Smuts, P. Walsh, K.A. Schug, Gas chromatography-vacuum ultraviolet detection for classification and speciation of polychlorinated biphenyls in industrial mixtures, J. Chrom. A. 2017, 1490, 191-200*





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