ARE YOU READY TO FLY! – JET FUEL ANALYSIS BY GC-VUV IS ABOUT TO TAKE OFF

The Standard Test Method for Determination of Saturated Hydrocarbon, Aromatic, and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV) ASTM D8267 (1) was recently published by ASTM as an official test method for the measurements of saturate, aromatic, and diaromatic content in aviation turbine fuels. The method has better correlation to the referee method for aromatics and diaromatics than any of the alternatives including SFC and HPLC with precision on average 5 to 10 times better than comparable ASTM methods. It requires no sample preparation or calibration, is automated, fast (14 minutes run time) and has one of the lowest costs of ownership per sample. In this article we look at the application and benefits of VUV spectroscopy for hydrocarbon type analysis for fuels in general and for aromatics in aviation turbine fuels in particular.

Why is Hydrocarbon Type Analysis so Important for Fuels?

Traditional crude oil derived gasoline and middle distillate fuels like kerosene, diesel and jet fuel are complex mixtures of hydrocarbon molecules which can be broadly classified by their structures such as normal paraffins, iso-paraffins, olefins, naphthenes and aromatics. These chemical types and their relative concentrations are important in determining the performance and stability of the fuels in use. For example, it has been shown that aromatics in jet fuel have an impact on the fine particle emissions and that the amount of sediment formed in fuels as a result of oxidation depends to a considerable extent on the concentration and structure of the aromatic hydrocarbon types present. Aromatics and iso-paraffins are used to increase octane number whereas olefins and diolefins have been linked to the formation of gums and varnishes which can lead to unwanted effects such as deposition in car filters, distribution lines, engine components and also the formation of sludge in engine oil. As a result, many fuel specifications, standards and standard methods have been developed for hydrocarbon type analysis over the years.

GC-FID and its limitations for Hydrocarbon Type Analysis

At a GC Symposium held in the fall of 1958 in Leipzig Denis Desty at British Petroleum was the first to report publicly on a gas chromatograph incorporating a capillary column and a flame ionisation detector (FID) for the analysis of hydrocarbon samples and since then this has been the technique of choice in the petroleum industry for the detailed molecular characterization of complex hydrocarbon samples such as gasoline and middle distillate fuels like diesel, kerosene and jet fuels.

The reason for this was the high resolving power of capillary GC, which allowed the identification of the compound based on retention time indices, combined with the high sensitivity, broad linear dynamic range and the relatively uniform response to hydrocarbons of the FID detector. However, the FID did have some drawbacks in that although the response is generally proportional to the mass of carbon present and was good for quantification it did not provide any information about the molecular structure and therefore the hydrocarbon type being detected. Therefore GC-FID methods for Hydrocarbon Type Analysis had to rely on either very high resolution long analysis time separations, or complex multi column switching systems and even then these were limited mainly to the gasoline boiling range. Comprehensive 2DGC with FID has been employed to extend the boiling range to middle distillates, but this has not yet found widespread application in routine petroleum analysis laboratories due to a number of factors including complexity, a range of instruments with no standard approach to modulation and also no commonly accepted protocol for data analysis and reporting software. Also, although comprehensive 2DGC does give greater resolution than single dimension separations, the detector is still the FID and therefore gives no information on molecular structure and coeluting peaks cannot be resolved.

The Power of Molecular Spectroscopy in the Vacuum Ultraviolet for Hydrocarbon Type Analysis

Molecular spectroscopy is the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by molecules, which may be in the gas, liquid, or solid phase and is one of the most commonly used approaches to classifying and quantifying molecular species based on their chemical structures. Molecular spectroscopy techniques such as NMR, FTIR, and UV/Vis have long been routinely employed in laboratories for decades, but now there is a new kid on the block in Vacuum Ultraviolet Spectroscopy (VUV).

Nearly all compounds absorb in the VUV region of the electromagnetic spectrum. The high energy, short wavelength VUV photons probe electronic transitions in virtually all chemical bonds including ground state to excited state $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$. The result is spectral "fingerprints" that are specific to individual compound structure and can be readily identified by the VUV spectral library. Until recently working with VUV Spectroscopy had historically been restricted to bright source synchrotron facilities due to significant background absorption challenges, but the introduction of the first bench-top spectrometer capable of full VUV spectrum detection in 2014 by VUV Analytics has led to the technique being widely available for routine use. The introduction of the technique as an affordable detector for gas chromatography was a major step in the availability of the technique for real world applications. The unique VUV spectra enable closely related compounds such as structural isomers to be clearly differentiated and it is this feature, combined with providing spectral information that is both qualitative and quantitative for most gas phase compounds, which makes VUV Spectroscopy coupled with GC such a powerful and unique tool which is revolutionising hydrocarbon type analysis for fuels and related products.

The VUV Analyzer™ for Fuels Platform

The VUV Analyzer is a platform developed for the analysis of fuels with value, ease-of-use, and flexibility in mind. The instrumentation can run multiple fuels related methods on one VUV Analyzer and allows users to rapidly switch between different analyses using the same GC, column, detector, and software. This simplifies operation for the analyst and accelerates analysis time across methods, including gasoline (ASTM D8071), jet fuel (ASTM D8267), diesel fuel, bromine number, diene value, and non-traditional gasoline additives (NTGA) screening, to name a few. All of these are achieved by simple applying the relevant method temperature programme and selecting the proper VUV Analyzer routine. This flexibility for routine analysis is unrivalled and in addition the instrument has great potential for application in non-routine investigational analysis such as looking for, identifying and quantifying contaminants and solving quality issues throughout the fuels manufacturing and supply chains.

The graphic in Figure 1 summarises the current range of applications which have been developed, or are currently in the final stages of development, for the VUV Analyzer for Fuels™.

So What is important about Hydrocarbon Type Analysis in Aviation Turbine Fuel?

According to ASTM (1) "The determination of class group composition of aviation turbine fuels is useful for evaluating quality and expected performance, as well as compliance with various industry specifications and governmental regulations." As mentioned earlier, the ability to accurately and precisely measure the concentration and type of aromatics present in jet fuel are not only important to meet regulatory requirements but also reduce the environmental impact and the prevention of sedimentation issues through oxidation. It has been reported that amount of sediment formed in fuels as a result of oxidation depends to a considerable extent on the concentration and structure of the aromatic hydrocarbons present in the fuels.

Why do we need a GC-VUV Method for Aviation Turbine Fuels?

The current ASTM referee method for testing aromatics in aviation turbine fuels and gasoline is ASTM D1319 -18 the Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (2). ASTM D1319 was originally developed in the early 1940s and approved as a standard method by ASTM in 1954. The method employs a calibrated glass column packed with activated silica gel topped with a mixture of fluorescent indicator dyes. The sample is adsorbed onto the silica gel and the hydrocarbon types are then eluted using alcohol. The fluorescent dyes separate selectively between the hydrocarbon types and quantification is dependent on the accuracy of identifying and recording of the fluorescent bands by eye. The method is tedious and labour intensive as sample preparation is time consuming, the chromatographic run is lengthy, and the column requires constant monitoring. Other limitations include poor reproducibility and the method is subject to operator bias as it relies on the analyst correctly identifying and physically measuring the separated bands.

Recently D1319 has come under serious scrutiny as the most recent batch of dyes is not fluorescing properly for middle distillates in the aromatics region which can make analysing jet fuel rather difficult (aromatics composing 10-25% of the total volume). Furthermore, the sole manufacturer of this dye no longer exists, and so far, the synthesis of the dye has not been successfully reproduced and the ASTM have had workgroups looking into the implications of this and proposing method modifications and developments. As a result of this activity ASTM D8267-19 (1) was approved as a standard procedure for the determination of saturated, aromatic, and diaromatic content in aviation turbine fuels. This novel method clearly demonstrates the power of molecular spectroscopy as a GC detection technique for hydrocarbon type analysis by providing a simple, automated GC analysis with minimal sample preparation in a run time of 14 minutes. At the time of writing, an updated version of the method along with its final research report, which removes references to saturates in the title and scope (as they are not in the jet fuel specification), was balloted on August 27th, 2019. Assuming no negatives that ballot will close after 30 days and the method will be approved with the permanent precision statement. After that the method will be petitioned for inclusion into ASTM D1655 which is expected to happen by the end of the year and readers are advised to consult the ASTM website regularly to ensure they are aware of the latest status.

Examples of gas phase VUV spectra for different hydrocarbon class types as shown in Figure 2, which shows that, in addition to individual components having unique compound-specific spectra providing provide excellent selectivity and unambiguous identification, the spectra demonstrate class similarities making hydrocarbon type classification a simple process.

Unlike any other technique proposed for aviation turbine fuel analysis these unique information rich spectra allow spectral deconvolution techniques to be applied to co-eluting compounds and the performance is further improved as the instrument software also uses the added time domain from the GC separation to improve performance using VUV's patented Time Interval Deconvolution technology(3). Having spectral data is also important in the case of a query in the event of any quality disputes as the spectral data can be retrospectively interrogated in great detail to reinforce and validate the correct identification and allocation of peaks.

Also, because we are dealing with spectroscopic data quantification (governed by the Beer Lambert Law), combined with the application specific spectral libraries and compositional reporting,

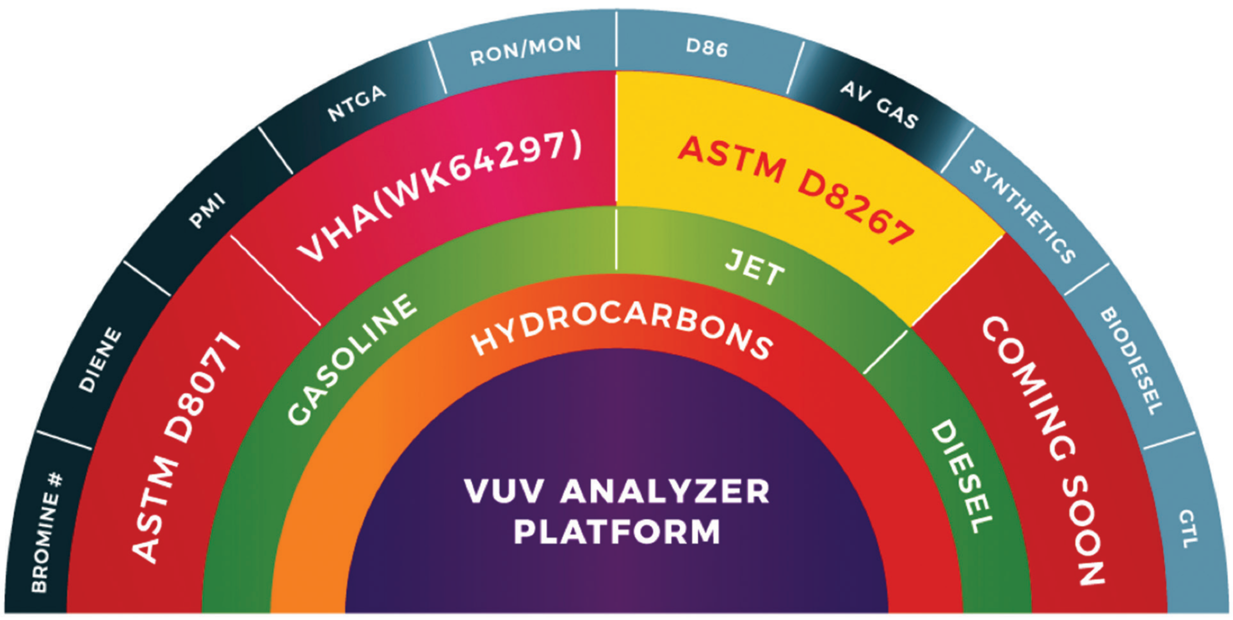


Figure 1: Graphic showing the current application areas and methods either already developed, or currently in the final stages of development, for fuels related applications.

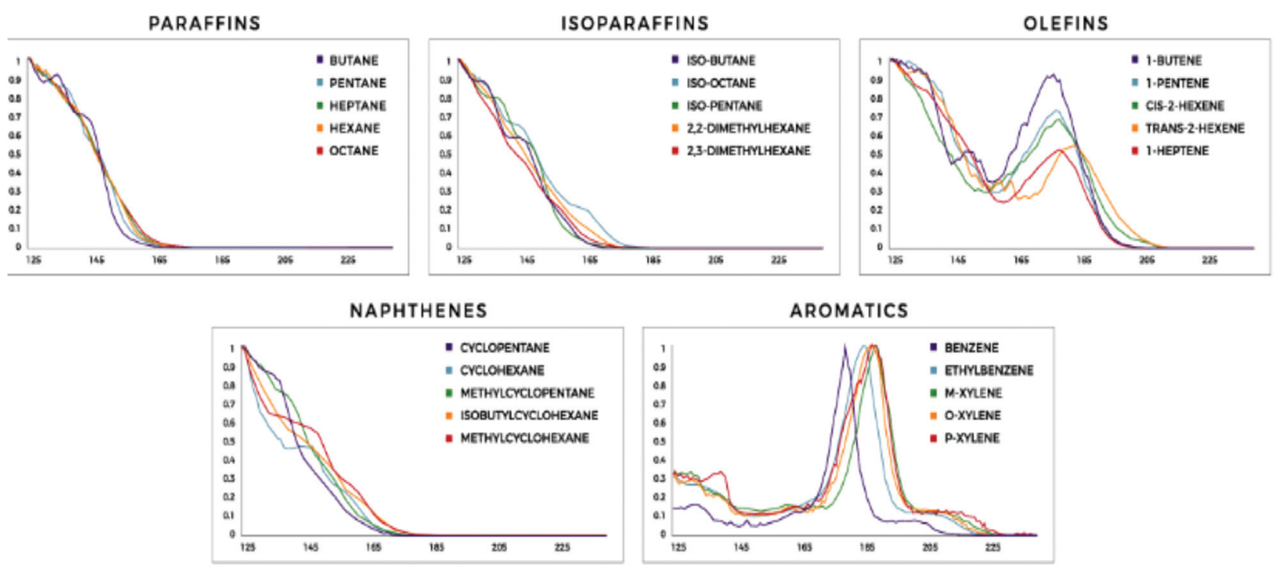
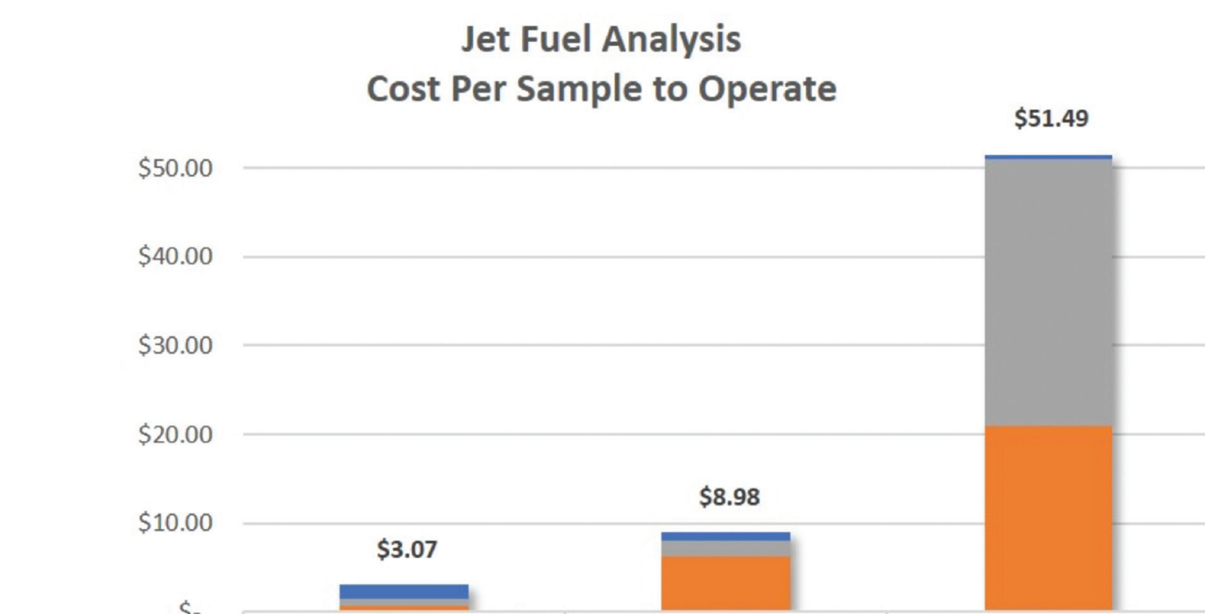


Figure 2: Example VUV Spectra showing unique compound specific and hydrocarbon class similarities for a selection of common molecules encountered in fuels



	ASTM D8267 (GC-VUV)	ASTM D6739 (HPLC)	ASTM D1319 (FIA)
Capital	$1.55	$1.01	$0.54
Labor	$0.83	$1.67	$30.00
Consumables	$0.68	$6.30	$20.96
Total cost/sample	$3.07	$8.98	$51.49

Figure 3: Cost pes sample comparison for GC-VUV with HPLC and SFC.

the instruments are in effect self-calibrated and requires no regular calibrations, (although users would be advised to run relevant check standards as part of their quality assurance programme).

Comparison of ASTM D8267-19 GC-VUV with Alternative Methods

In addition to the reference ASTM D1319 and ASTM D8267 method there are 2 other ASTM proposed methods at the time of writing: one, based on ASTM D5186 (4), employs Supercritical Fluid Chromatography with FID detection using supercritical carbon dioxide as the eluant and the other (ASTM D6379) based on normal phase HPLC with heptane as the eluant and refractive index detection (5). These both employ low resolution class type separations using retention time cut points to identify hydrocarbon class types and have no capability for spectral validation of the species measured.

Accuracy and Precision: In a correlation study, results obtained from GC-VUV (ASTM D8267), SFC and HPLC (ASTM D6379) were compared to the expected results from reference methods ASTM D1319 for Total Aromatics and ASTM D1840 (5) for Di-Aromatics. In all cases the GC-VUV method ASTM D8267 has better correlation to the referee methods than any of the alternatives.

In addition, based on an interlaboratory study (ILS) to determine repeatability (r) and reproducibility (R) in accordance with D6300 requirements the precision of GC-VUV ASTM D8267 was shown to be on average five (5) to ten (10) times better than comparable methods.

Cost of Ownership and Cost per Sample: The GC-VUV method runs on the VUV Analyzer platform which we have already shown is capable of running a plethora of fuel related analysis under full automation and users can seamlessly combine analyses of jet fuels, finished gasolines and even diesel fuels in sequences without the need to change hardware or setup. This means that by using the same instrument for all analysis ultimately reduces complexity, increases efficiency and provides better data quality and consistency. A typical cost per sample breakdown based on equipment, labour and consumables and maintenance is shown in Figure 3. On average, in terms of operating costs on a per sample basis, running ASTM D8267 on the VUV Analyzer platform costs 2x less in labor and 9x less in consumables per sample than the alternative HPLC method and 15x less in labor and up to 60x less in consumable cost per sample than the reference fluorescent dye method.

Closing Comments and Conclusions

For almost 60 years GC with FID has arguably been the dominant technique for the routine analysis of crude oil derived fuels but that is now changing dramatically with the development and introduction of the VUV gas phase detector which couples seamlessly with GC and is revolutionizing the analysis of light and middle distillate fuels across the board. It is a universal detector which, due to the unique compound specific spectra obtained combined with utilizing common spectral features for hydrocarbon classes, allows hydrocarbon type identification and quantification in a way which has previously not been possible.

Since its introduction in 2014 the application space of the VUV detector for GC has grown so much that the company now provides a dedicated VUV Analyzer™ for Fuels capable of providing a range of fuel analyses which comply with ASTM standard methods. In fact, gaining approval for so many standard methods in such a short time is a testament to the power and applicability of the technique. All methods offered are fully developed, calibrated, and automated and can be readily be run by process operators in an open access type of environment if required. The indication is that there will be many more applications to come in the future and I can see this becoming an increasingly powerful tool as the industry continues to move to new and renewable fuel sources.

In addition, due to the power of time resolved spectral deconvolution (3) to identify and individually quantify co-eluting peaks it is often not necessary to achieve complete chromatographic resolution which means many methods can be run faster thus improving sample throughput and turnaround.

In many cases the data provided by GC-VUV is better or comparable in terms of accuracy and precision with conventional methods and correlates well with current reference methods. In particular the performance to date for the analysis of aromatics in aviation turbine fuel shows superior performance to alternative techniques not only in result quality but also in turnaround times and cost per sample. The fact that in many laboratories one GC-VUV Fuels analyser could replace many single application GC-FID instruments means every lab manager should be seriously considering the impact it could have on their operations.

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References

(1) ASTM D8267-19, Standard Test Method for Determination of Saturated Hydrocarbon, Aromatic, and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV), ASTM International, West Conshohocken, PA, 2019, www.astm.org

(2) ASTM D1319-18, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption, ASTM International, West Conshohocken, PA, 2018, www.astm.org

(3) Rapid Analysis and Time Interval Deconvolution for Comprehensive Fuel Compound Group Classification and Speciation Using Gas Chromatography–Vacuum Ultraviolet Spectroscopy Phillip Walsh, Manuel Garbalena, and Kevin A. Schug: Anal. Chem. 2016, 88, 11130–11138

(4) ASTM D5186-19, Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography, ASTM International, West Conshohocken, PA, 2019, www.astm.org

(5) STM D6379-11(2019), Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection, ASTM International, West Conshohocken, PA, 2019, www.astm.org

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