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Application Benefits

- Achieves both qualitive and quantitative analysis of total aromatics, monoaromatics, and diaromatics using the VUV Analyzer™ Platform.
- Accurate analysis due to spectral verification.
- 5–10 times better precision, repeatability and reproducibility than alternative approaches, FIA and HPLC.
- No sample preparation or calibration curves.
- Rapidly separate and quantify key classes of compounds (14-minute run time).
- Automated analysis and reporting using VUV Analyze™ Software.
- Fully compliant with ASTM D8267.
- Cited in ASTM D1655 and the Canadian General Standards Board (CGSB) Aviation Turbine Fuel Specifications as an alternative to ASTM D1319 for total aromatics.
- Cited in ASTM D3338 as an approved method for calculating Net Heat of Combustion.
- Does not require the use of dyes or hazardous solvents.
- 2.5–16 times lower total cost to operate than alternative approaches – FIA and HPLC, respectively.

VUV Analytics Solutions

- VUV Analyzer[™] Platform for Fuels
- VGA-100[™] Vacuum Ultraviolet Spectrometer
- VUVision[™] Software
- VUV Analyze[™] Software
- VUV Jet Fuel Application

KEYWORDS -

Aviation turbine fuel, Jet fuel, vacuum ultraviolet spectroscopy, VUV, VGA, aromatics, monoaromatics, diaromatics, saturates, naphthalenes, D8267, D1319, D1840, D6379

INTRODUCTION

Aromatic hydrocarbons are limited (25% vol max) in jet fuel for a variety of reasons. First, since they emit more radiant energy during combustion, high concentrations can have an adverse effect on the performance and safety of jet engines. Second, aromatic hydrocarbons produce more smoke and harmful particulate emissions which has an impact on the environment. Aromatic content must also be kept to a minimum value in order to maintain elastomer compatibility and energy density.

Currently, there are several established product specifications, including ASTM Standard D1655 and the British Ministry of Defence (MoD) Defence Standard (DEF STAN) 91-091, that are intended to regulate and limit the presence of aromatic compounds. These standards define the methods and technologies that can be used for testing and certification purposes.

Traditionally, both Fluorescence Indicator Absorption (FIA) and High-Performance Liquid Chromatography (HPLC) have been used to analyze aromatic content in jet fuel. Both the FIA (ASTM D1319) and HPLC (ASTM D6379) methods have had a long history of jet fuel analysis. FIA has been available since the early 1950s and has changed little since it was first adopted. While considered an "easy" approach, it is manual and laborious and relies on the ability of the analyst to accurately measure (with a ruler) fluorescent dye bands. Because of the hands-on nature of this technique, the number of samples that can be analyzed is limited to the capacity of the test apparatus and availability of a technician. The method is prone to human error and poor precision.

HPLC is a newer approach. While HPLC is a major step forward compared to FIA it is not without its complexities. This method requires sample preparation, calibration standards, and the need for hazardous solvents like heptane. Additionally, results must be converted by the user from mass % to volume % in order to comply with jet fuel specifications. While an improvement over FIA, it is also time intensive and requires a skilled analyst.

This application note describes a new approach for the analysis of jet fuel using Gas Chromatography (GC) combined with Vacuum Ultraviolet Spectroscopy (VUV) and a newly approved alternative GC-VUV method – ASTM D8267.



Experimental

GC Conditions

Injection Volume: 1μL Inlet Temperature: 250°C Split Ratio: 100:1 Column: 100% non-polar PDMS Column (30m x 0.25, 0.25 μm) Carrier gas: Helium Oven Program: 50°C, hold 0.1 min; 15°C/min to 260°C Run Time: 14 minutes

VGA Conditions

Makeup Gas Pressure: N2 (pressure determined on instrument) Flow Cell Temperature: 275°C Transfer Line Temperature: 275°C Acquisition Frequency: 7 Hz Acquisition Range: 125-240 nm

RESULTS AND DISCUSSION

A simple five-step analytical workflow (Figure 1) was employed to compounds of interest present in a variety of jet fuel samples. The jet fuel samples did not require any special sample preparation and were run on a VUV Analyzer Platform for Fuels consisting of a VGA-100[™] Spectrometer coupled with a Gas Chromatograph using both VUVision[™] Software and VUV Analyze[™] Software configured to run ASTM D8267.

1	SYSTEM VALIDATION	Single standard is used to check split linearity and baseline. Automated RI file generation and reporting.	
2	SAMPLE PREPARATION	No sample preparation is required with this application.	
3	DATA ACQUISITION	All data is acquired using VUVision Software and is automated. No calibration curve required.	
4	SPECTRAL MATCHING	Automated with VUV Analyze Software running the Jet Fuel Application for ASTM D8267.	
5	QUANTITATION	Automated with VUV Analyze Software. Relative Response Factors > mass %. Densities > volume %.	



GC-VUV was used to acquire and analyze a variety of jet fuel samples, including a conventional sample shown in Figure 2 (VUV-QCJ), an alternative jet fuel with no aromatic content shown in Figure 3, and a sample (AITF T296) spiked with di-aromatic content shown in Figure 4. Saturate, mono-aromatic and di-aromatic content are easily visible using specific portions of the acquired wavelength range, referred to as spectral filters. However, the entire wavelength range is used when performing spectral matching and quantitation.



Figure 2 - Conventional jet fuel sample with spectral filters overlaid for Saturates (125 – 160 nm), Mono-aromatics (175 – 205 nm), and Di-aromatics (200 – 240 nm).







Figure 4 - High aromatic content sample. Mono and Di aromatics is easily filtered.

Unlike traditional chromatography, where components of interest are identified and quantified using peak retention time and peak integration, data analysis in GC-VUV uses spectral validation based on a library of compounds. Saturate, mono-aromatic, and di-aromatic compounds have distinct spectral shapes, which provides reliable quantification with spectral confirmation. Additionally, compound classes share spectral similarities which allows them to easily be combined for accurate class-based reporting.

Coeluting compounds can be spectrally distinguished using Time Interval Deconvolution[™] (TID[™]). With TID, each chromatogram is divided into time intervals, and the spectrum at each time interval is matched against the library. Figure 5 shows the acquired spectrum at 9.1 minutes. This spectrum shows a clear coelution. When a coelution occurs, TID takes advantage of the unique spectral shapes of each class to determine the best multi-analyte fit as shown in Figure 6.



Figure 5 - Acquired spectrum at time interval 9.1 minutes.



Figure 6 - Spectral matching to deconvolve coeluting peaks.



All results are reported using the VUV Analyze Software based on compound class. Figure 7 shows the report for the VUV-QCJ sample discussed above. The table (1) provides reported values in both mass % and volume % for total aromatic, mono-aromatic, di-aromatic, and saturate content.

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Chromatographic overlays (2) are provided for easy visual distinction of mono-aromatic, di-aromatic, and saturate content. Additionally detailed acquisition information (3) is provided for analysis traceability.

ASTM D8267 Report File



Figure 7 - Typical report for GC-VUV running ASTM D8267. Compound classes are reported in the table (1) while chromatographic overlays (2) are provided for visual distinction of mono-aromatic, di-aromatic, and saturate content. Detailed acquisition information (3) is provided for analysis traceability.



METHOD SCOPE

The scope of ASTM D8267 is shown in the following (Table 1):

Table 1 - ASTM D8267 Method Scope

COMPOUND CLASSES	MIN VOL %	MAX VOL %
TOTAL AROMATIC COMPOUNDS	0.487	27.876
TOTAL MONOAROMATIC COMPOUNDS	0.49	27.537
TOTAL DIAROMATIC COMPOUNDS	0.027	2.523

PRECISION, REPEATABILITY (r), AND REPRODUCIBILITY (R)

Precision for ASTM D8267 was determined by an interlaboratory study (ILS) that included 10 laboratories and 24 samples. This ILS included a variety of jet fuel types including JA, JA1 and F24 along with samples generated from different refining processes and sustainable alternative jet fuels. Supporting data for this ILS may be obtained from ASTM by requesting Research Report RR:D02-D1911.

Additionally, other studies have been conducted as further validation of the precision, repeatability and reproducibility claims. Specific studies include 12 samples from a U.S. DoD ILS, 13 samples from a study conducted by Valero, and 12 samples from a Southwest Research Institute study comparing old versus prototype FIA dyes for ASTM D1319.

The data from the 65 samples used across these studies is summarized in Figure 8. The consolidated graph shows the ASTM D8267/D1319 data pairs and linear trendline all of which are well within the reproducibility of ASTM D1319 indicated by the upper and lower dotted lines (blue).



Figure 8 - Consolidated study comparing ASTM D8267 reproducibility with ASTM D1319.



Jet fuel analysis using the VUV Analyzer[™] for Fuels running ASTM D8267 demonstrates up to 10 times better repeatability and reproducibility compared to the referee method (D1319) and the HPLC alternative method (D6379). Figure 9 compares the precision across these methods for a conventional jet fuel with approximately 18% total aromatics.



Figure 9 - Comparison of method precision.

COST PER ANALYSIS

Cost-per-analysis using GC-VUV running ASTM D8267 is significantly less on a per sample basis than the traditional approaches (ASTM D1319 and D6379). This is due in large part to lower labor overhead resulting from the elimination of sample preparation and complex apparatus setup, the implementation of rapid acquisition and analysis times, and the automation provided by the VUV Analyze Software along with minimal ongoing consumable and maintenance costs.

To better compare cost-per-analysis, GC-VUV (ASTM D8267) was compared to both ASTM D1319 and ASTM D6379. To ensure a consistency, the parameters used in the calculations included: capital cost of the analytical hardware depreciated over five (5) years, a consistent utilization rate of 80% across all techniques, expected annual consumable and maintenance costs across all techniques, and finally the cost of labor and labor time spent per day interfacing with a given technique.



Figure 10 outlines the results of that analysis and shows a dramatic difference in cost-per-analysis between the different methodologies. FIA (ASTM D1319), while having the lowest capital cost, is the most expensive technique to operate on a per sample basis. This is due in large part because of the need to prepare the apparatus, ongoing consumable costs (columns, dye, packing material), and lengthy run times which require hands-on attention. Overall, running FIA and ASTM D1319 can cost \$51.49 USD per sample.

HPLC (ASTM D6379) has a significantly lower cost-per-analysis cost compared to FIA. Capital costs are higher than FIA. However, due to the need for complex sample preparation, the expense associated with hazardous solvent disposal, more maintenance costs, and more labor overhead this technique costs approximately \$8.98 USD per sample to operate.

GC-VUV running ASTM D8267 by contrast only costs approximately \$3.07 USD per sample to operate. This is 2.5 times less expensive than HPLC and 16 times less expensive than FIA. This difference is due to the fact that with GC-VUV running ASTM D8267 labor costs are reduced because there is no sample preparation and analysis is completely automated. Additionally GC-VUV analysis of jet fuel only takes 14 minutes per sample. This means that a single GC-VUV has higher sample capacity than the other approaches which provides more throughput with fewer analytical systems. Finally, GC-VUV has minimal consumable and maintenance costs.



Figure 10 - Cost-per-sample analysis. Note that all values are in USD.



CONCLUSIONS

The combination of the VUV Analyzer[™] for Fuels (GC-VUV) and ASTM D8267 measures the aromatic content (total aromatics, monoaromatics, and diaromatics) of jet fuel with significantly better Precision, Repeatability (r) and Reproducibility (R) than the existing alternatives – FIA (ASTM D1319) and HPLC (ASTM D6379).

Jet fuel analysis using the VUV Analyzer for Fuels is fast. Acquisition and analysis only takes 14 minutes.

Jet fuel analysis is significantly easier using the VUV Analyzer Platform running ASTM D8267 because the hardware setup is simple, there is no need for sample preparation or calibration curves, and analysis is completely automated.

Results are reported in a simple, easy-to-consume report format that clearly identifies quantified results in both volume and mass percent and provides chromatographic overlays for visual distinction.

Running the VUV Analyzer for Fuels and ASTM D8267 is 16 and 2.5 times less expensive to operate compared to FIA (ASTM D1319) or HPLC (ASTM D6379), respectively.

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