VUV ANALYTICS

AUTOMATED ANALYSIS OF THE TOTAL AROMATIC, POLYAROMATIC, AND FATTY ACID METHYL ESTER (FAME) CONTENT OF DIESEL FUELS USING GC-VUV

Application Benefits

- Achieves both qualitative and quantitative analysis of total aromatics, polyaromatic hydrocarbons (PAHs), and fatty acid methyl esters (FAME) using a single-injection, automated technique on the VUV Analyzer™ Platform.
- Capable of analyzing conventional, renewable, and synthetic diesel fuels as well as biodiesel blends.
- Accurate analysis with spectral validation.
- No sample preparation or calibration curves.
- Rapidly separate and quantify key classes of compounds (25-minute run time).
- Automated analysis and reporting using VUV Analyze™ Software.
- Fully compliant with ASTM D8368.
- Does not require the use of dyes or hazardous solvents.

VUV Analytics Solutions

- VUV Analyzer™ Platform for Fuels
- VGA-100™ Vacuum Ultraviolet Spectrometer
- VUVision™ Software
- VUV Analyze™ Software
- VUV Diesel Application

KEYWORDS

Diesel, biodiesel, vacuum ultraviolet spectroscopy, VUV, VGA, aromatics, polyaromatics, fatty acid methyl esters (FAMEs)

INTRODUCTION

The combustion properties of diesel fuel and the resulting emissions from their consumption is greatly influenced by the percentage of aromatic hydrocarbons that are present. As a result, measuring the aromatic content of diesel fuels is important not only to determine the quality of the fuel from a manufacturing standpoint, but also to comply with environmental regulations for air quality and emissions. For example, both the United States Environmental Protection Agency (USEPA) and the California Air Resources Board (CARB) place limits on the total aromatic content and polynuclear aromatic content in diesel fuels. Complying with these regulations while maintaining process and quality control requires robust and precise analytical methods.

While it is important to measure aromatic hydrocarbons, modern diesel fuels are often blended with as much as 20% (B20) biodiesel. As a result, it is also important to measure the fatty acid methyl esters (FAMEs) content to ensure compliance with current diesel fuel specifications.

Several methods have been developed to measure either the aromatic content or FAME content of diesel fuel. These methods are summarized in Table 1. Analyzing both parameters has traditionally required the use of multiple analytical techniques and methods which adds complexity and cost to this type of analysis.

ASTM METHOD	D1319	D5186	D6591	D7371	D8368
TECHNIQUE	FIA	SFC	HPLC	FTIR-ATR-PLS	GC-VUV
Mono-aromatics		X	X		X
Di-Aromatics			X		X
Tri+ Aromatics			X		X
PAHs		X	X		X
Total Aromatics	Vol % only	X	X		X
FAMEs	N/A	N/A	N/A	1-20% vol	1-20% vol

Table 1: Several diesel test methods and the parameters they measure. ASTM D5186 and ASTM D6591 require special vol% calibration.

This application note describes a new approach for the analysis of traditional diesel and biodiesel fuel blends using a single analytical technique, Gas Chromatography (GC) combined with Vacuum Ultraviolet (VUV) Spectroscopy, and a single method, ASTM D8368.

Experimental

GC Conditions

Injection volume: 1 µL
Inlet temperature: 300 ˚C
Split ratio: 100:1
Column: 100% non-polar PDMS Column (30m x 0.25 x 0.25µm)
Carrier gas: Helium; 1ml min
Oven Program: 50 ˚C, hold 0.1 min; 15 ˚C/min to 260 ˚C, hold 10.9 min
Run Time: 25 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 five-step analytical workflow (Figure 1) is employed to analyze a conventional biodiesel blend. In contrast to alternative techniques which require sample dilution, analyzing diesel and biodiesel fuels using the VUV Analyzer for Fuels running ASTM D8368 is a direct-injection technique and requires no sample preparation.

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 Diesel Application for ASTM D8368.
5	QUANTITATION	Automated with VUV Analyze Software. Relative Response Factors > mass %. Densities > volume %.

Figure 1: Analytical workflow for GC-VUV diesel analysis using ASTM D8368

Data acquisition and analysis is carried out using the VUV Analyzer for Fuels consisting of a VGA-100 Spectrometer coupled with a gas chromatograph, and both VUVision Software and VUV Analyze Software configured to run ASTM D8368.

Instrument preparation requires running a system validation mixture. This is a certified gravimetric standard manufactured in compliance with ISO 17034 containing known quantities of linear alkanes (C7 to C30) and compound class markers. This system validation mixture is used to automatically create a retention time marker file and to assess split linearity.

RESULTS AND DISCUSSION (cont.)

Following system validation, the GC-VUV system is used to acquire and analyze a conventional biodiesel chromatogram from a sample known as VUV-CSD.

Data acquisition takes approximately 25 minutes per sample, and post-processing takes approximately 60 seconds. Post-processing is an automated process using VUV Analyze Software in which each chromatogram is divided into 2400 equally spaced time intervals. Each of those time intervals is then analyzed independently with each overlapping spectra deconvolved, identified, and then quantified using an approach called Time Interval Deconvolution™.

In contrast to traditional chromatographic techniques which require compounds of interest be identified and quantified using peak retention time and integration, GC-VUV provides data in three dimensions – column retention time, absorbance, and spectral response over a wavelength range. GC-VUV uses spectral validation based on a library of compounds in which each compound class has a unique spectral shape yet demonstrates spectral similarities among compounds of the same class. This enables accurate class-based reporting. Figures 2 through 8 show a single chromatogram with highlighted compound classes and some examples of their spectral similarities.

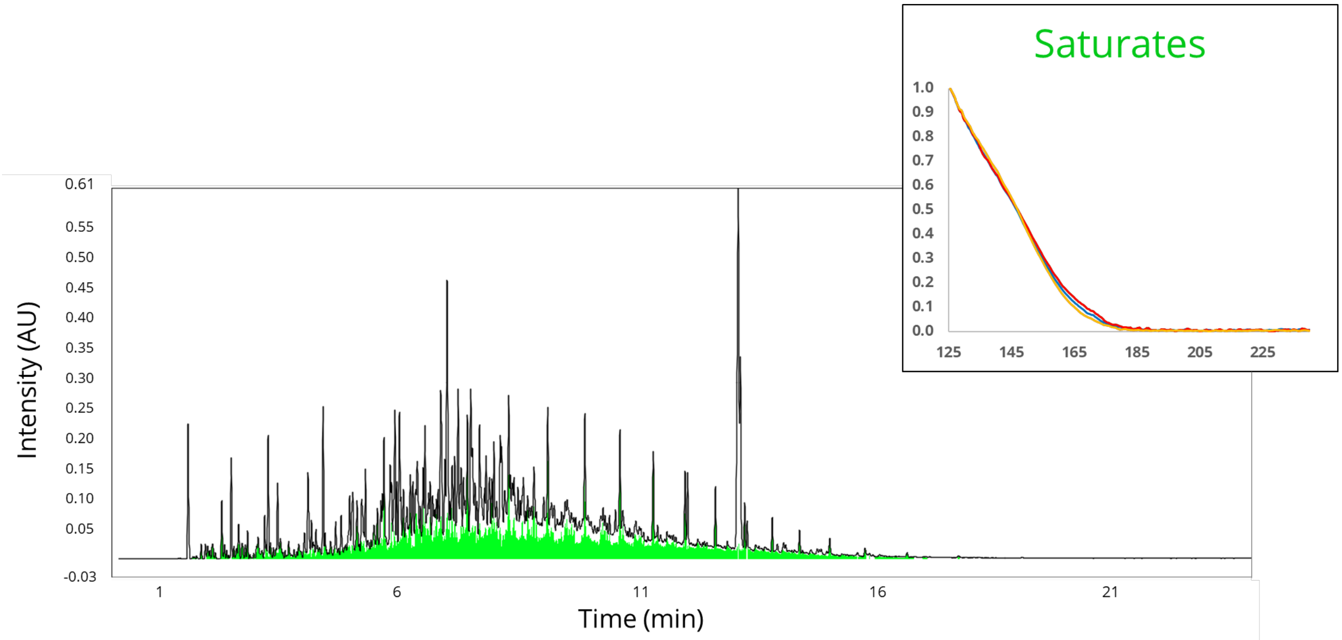

Figure 2: Chromatogram of a conventional biodiesel blend with the saturate spectral filter applied. The inset shows the VUV absorbance spectra of several common saturate compounds found in diesel fuel.

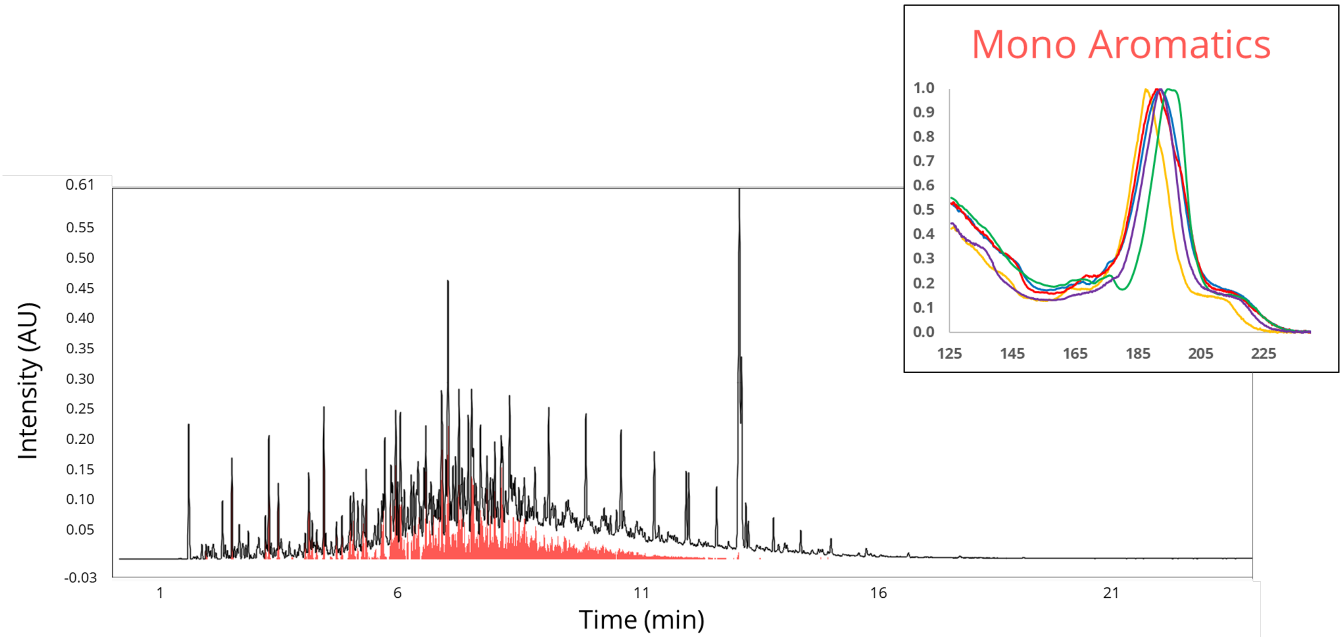

Figure 3: Chromatogram of a conventional biodiesel blend with the mono-aromatic spectral filter applied. The inset shows the VUV absorbance spectra of several common monoaromatic compounds found in diesel fuel.

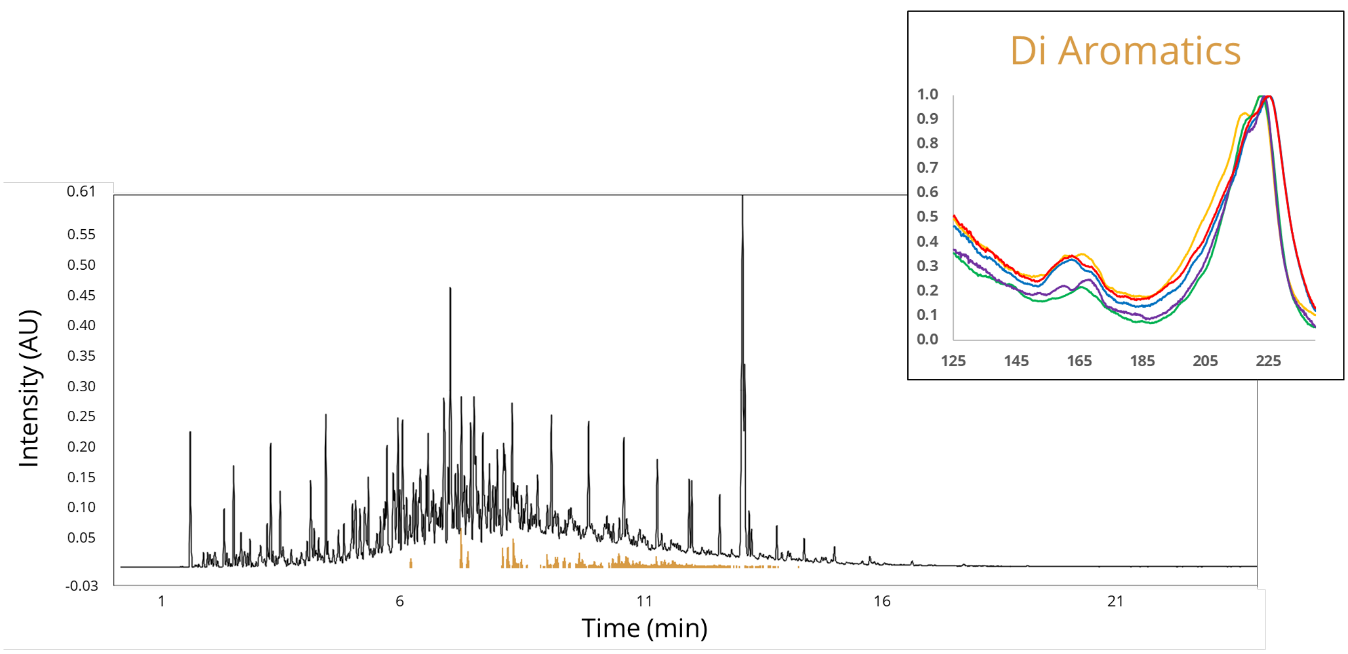

Figure 4: Chromatogram of a conventional biodiesel blend with the di-aromatic spectral filter applied. The inset shows the VUV absorbance spectra of several common di-aromatic compounds found in diesel fuel.

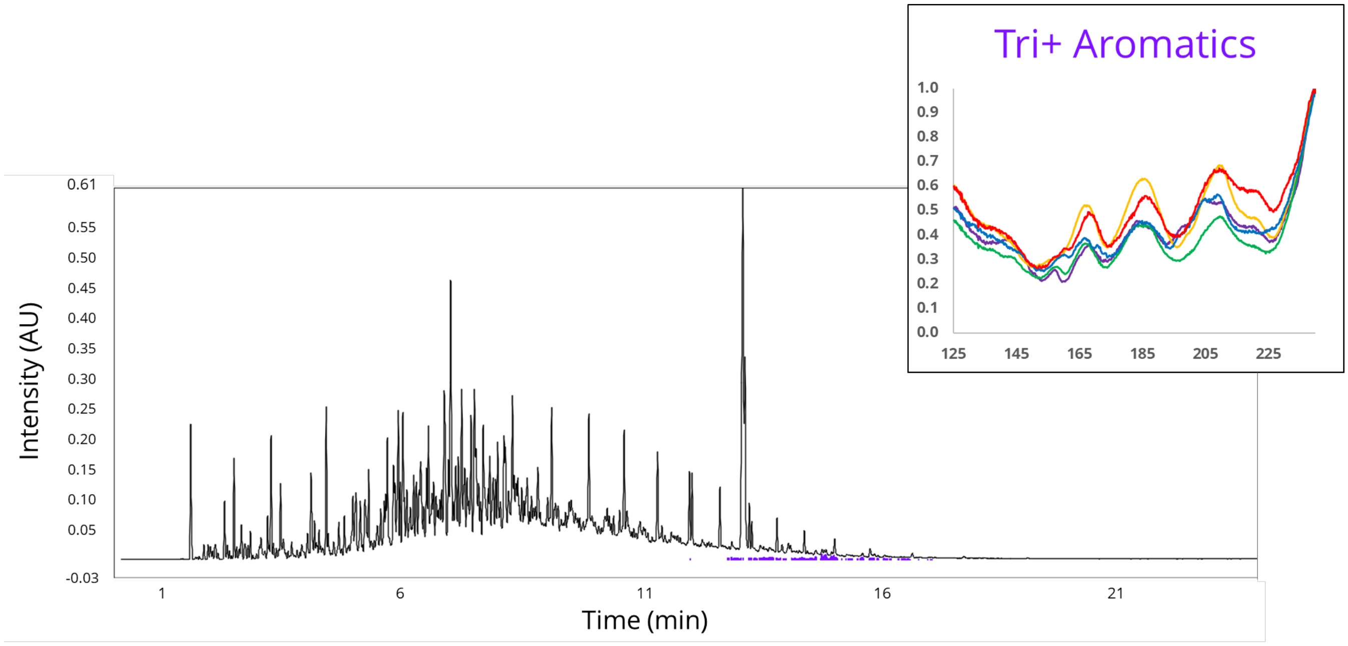

Figure 5: Chromatogram of a conventional biodiesel blend with the tri+ aromatic spectral filter applied. The inset shows the VUV absorbance spectra of several common tri+ aromatics found in diesel fuel.

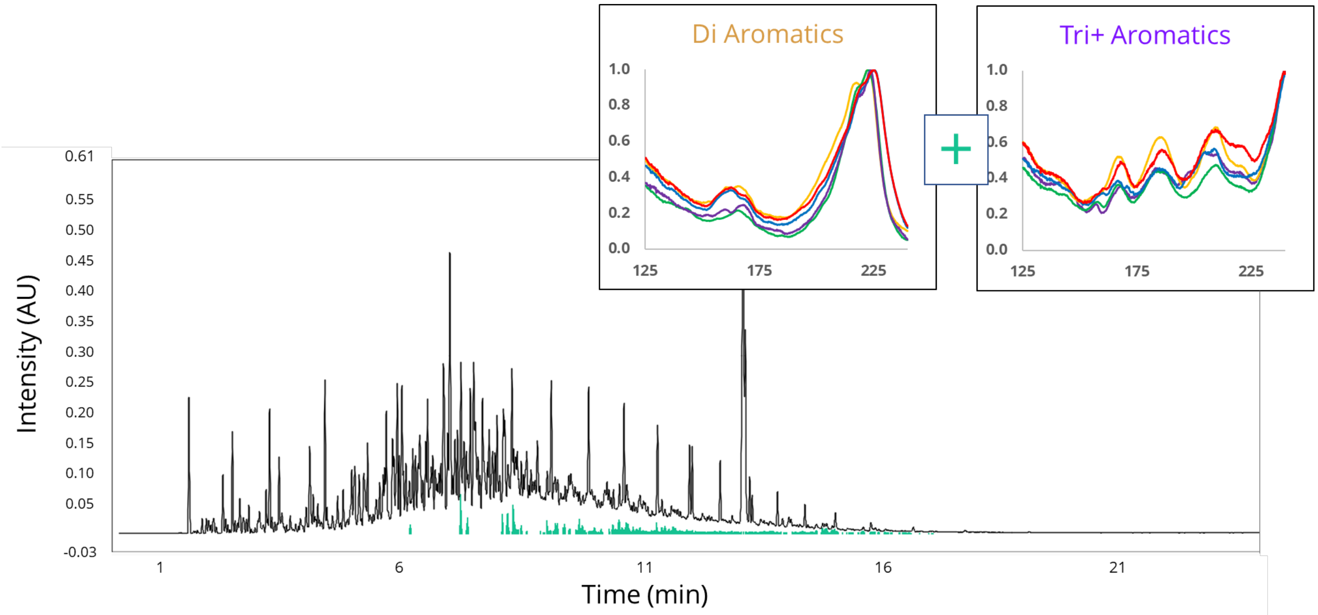

Figure 6: Chromatogram of a conventional biodiesel blend with the PAH spectral filter applied.

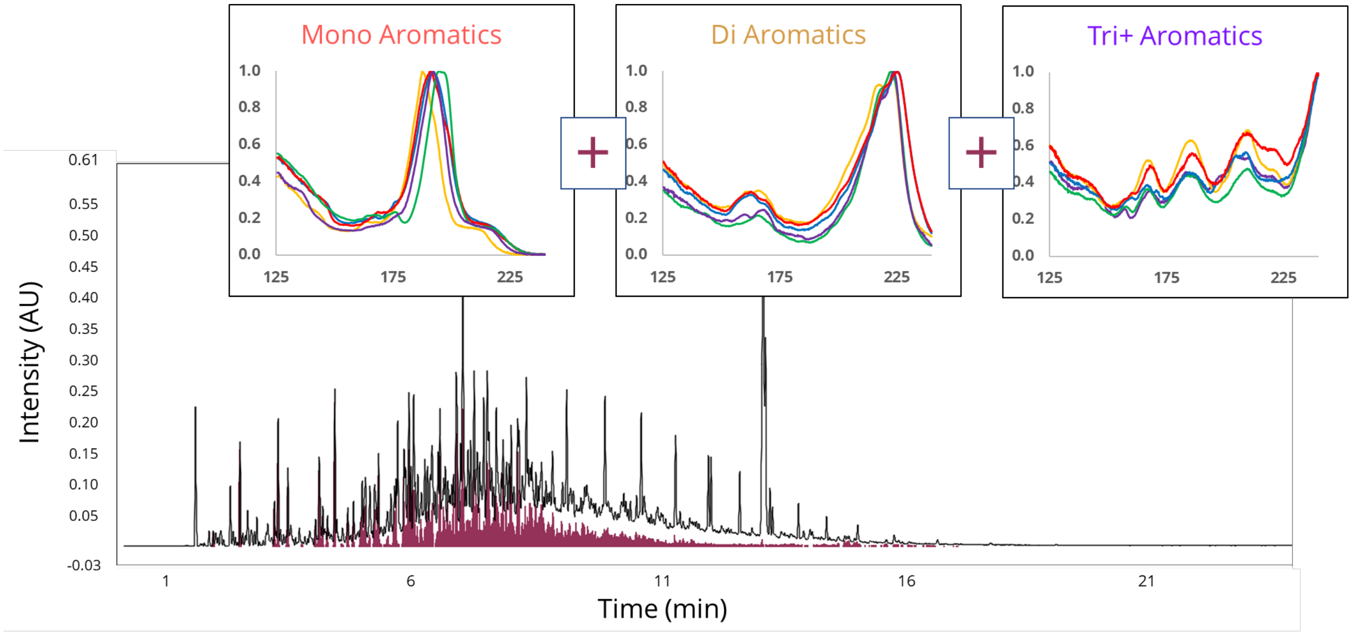

Figure 7: Chromatogram of a conventional biodiesel blend with the total aromatic spectral filter applied.

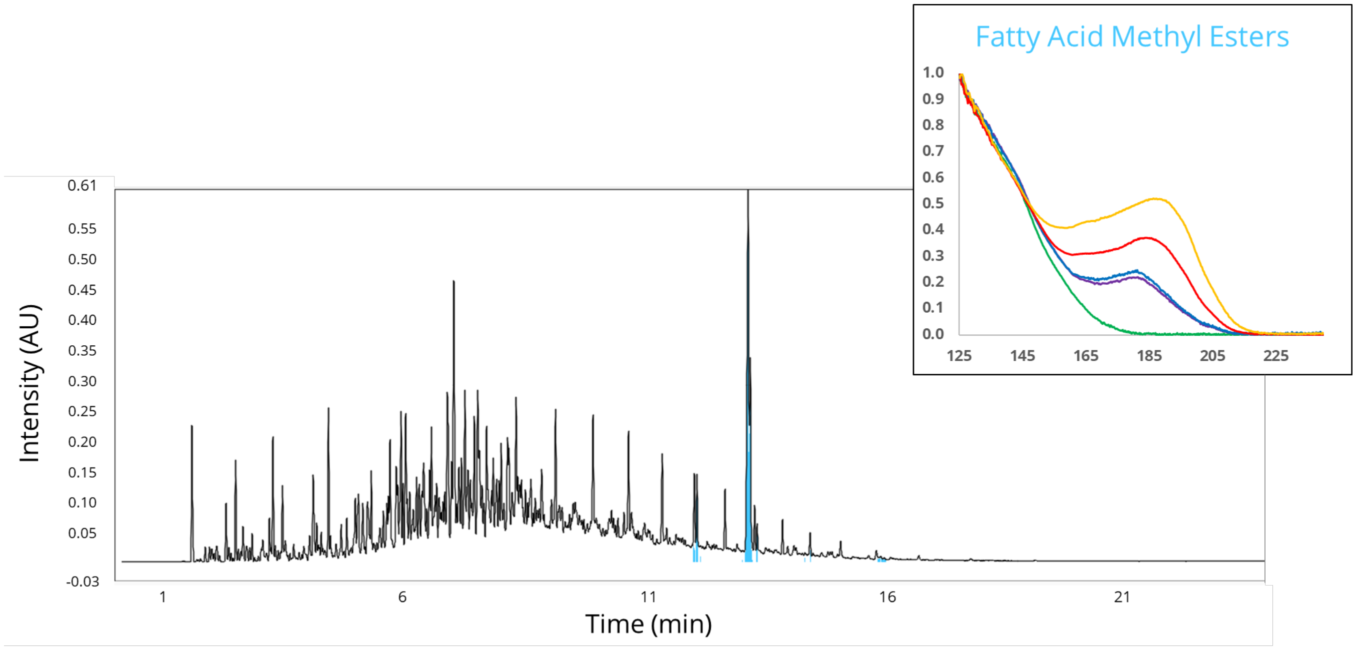

Figure 8: Chromatogram of a conventional biodiesel blend with the FAMEs spectral filter applied. The inset shows the VUV absorbance spectra of several several representative feedstocks including CME, SME, RME, and TME.

The results of the diesel analysis using GC-VUV and the Diesel Analyze Application are shown in Table 2. All parameters are reported in volume percent and mass percent.

CATEGORY	VOLUME %	MASS %
Total Saturates	71.8156	69.4367
Total Aromatics	23.2108	25.0496
Total Mono-Aromatics	21.8406	23.3264
Total PAHs	1.3702	1.7233
Total Di-Aromatics	1.1082	1.3803
Total Tri(+)-Aromatics	0.2620	0.3430
Total FAMEs	4.9736	5.5136

Table 2: Results of an analysis of diesel fuel using ASTM D8368.

Carbon number breakdown by class is also reported with both volume-percent and mass-percent results provided. Table 3 shows the volume percent breakdown of the VUV-CSD sample.

C#	TOTAL SATURATES	TOTAL AROMATICS	TOTAL MONO-AROMATICS	TOTAL DI-AROMATICS	TOTAL TRI(+)-AROMATICS	TOTAL PAHs	TOTAL FAMEs	TOTAL
C1-C5								
C6	0.2473	0.0361	0.0361					0.2835
C7	0.9138	0.2463	0.2463					1.1601
C8	1.6421	0.6034	0.6034					2.2455
C9	1.7471	0.9559	0.9559					2.7030
C10	2.8938	1.3584	1.3451	0.0133		0.0133		4.2522
C11	5.4398	3.13	3.0339	0.0962		0.0962		8.5699
C12	5.8022	5.2857	5.1273	0.1583		0.1583		11.0879
C13	10.2755	3.9538	3.6775	0.2764		0.2764		14.2294
C14	7.6295	3.0157	2.8634	0.1523		0.1523		10.6452
C15	10.0691	1.6959	1.6926		0.0032	0.0032		11.7649
C16	7.9786	1.2151	1.1852	0.0054	0.0245	0.0299		9.1937
C17	4.4697	0.8539	0.6676	0.1761	0.0101	0.1862	0.5479	5.8714
C18	3.4063	0.435	0.2496	0.1452	0.0402	0.1854		3.8413
C19	2.5743	0.1873	0.1012	0.0458	0.0403	0.0861	4.3812	7.1428
C20	1.9718	0.1498	0.0468	0.0186	0.0844	0.103		2.1216
C21	1.7648	0.0491	0.0014	0.0202	0.0275	0.0477	0.0444	1.8583
C22	1.1367	0.0308		0.0005	0.0303	0.0308		1.1675
C23	0.8856	0.0086	0.0071		0.0015	0.0015		0.8942
C24	0.5216							0.5216
C25	0.3847							0.3847
C26	0.0577							0.0577
C27	0.0035							0.0035
Total	71.8156	23.2108	21.8406	1.1082	0.262	1.3702	4.9736	100

Table 3: Carbon number breakdown of the VUV-CSD sample reported in volume percent. Note that the "Totals" column is the summation of the "Total Saturates", "Total Aromatics", and "Total FAMEs" parameters. Total Saturates are reported. However, precision has not been calculated for this parameter.

METHOD SCOPE

The scope of ASTM D8368 is shown in Table 4.

MATRIX	PROPERTY	UNITS	MIN	MAX	REPLACES METHODS	APPROVALS
	TOTAL AROMATICS	vol%	0.088	77.00	ASTM D1319, D5186, D6591, D7371	
DIESEL FUEL, B1-B20	TOTAL AROMATICS	mass%	0.104	79.451		
GTL	MONOAROMATICS	mass%	0.076	67.848		ASTM D975 ballot pending.
HVO	DIAROMATICS	mass%	0.027	34.812		
nC7 (98 °C) and nC30 (450 °C)	TRI+ AROMATICS	mass%	0.45	6.77		Pending CEN
	PAH	mass%	0.028	41.586		
	FAME	vol%	1.08	21.67		

Table 4: ASTM D8368 method scope.

CONCLUSION

The VUV Analyzer for Fuels configured for ASTM D8368 measures the saturates, total aromatics (mono-, di-, tri+, poly-) and FAMEs in diesel and biodiesel fuels with an easy-to-use approach.

Determination of total saturate, aromatic, polyaromatic, and fatty acid methyl ester (FAME) content can be accomplished with a single analysis.

Diesel fuel analysis using the VUV Analyzer for Fuels is fast. Acquisition and analysis only takes 25 minutes.

The VUV Analyzer for Fuels running ASTM D8368 can analyze both diesel and biodiesel blends with no changes to configuration or analysis parameters.

The VUV Analyzer for Fuels is capable of following standard methods ASTM D8071, D8267, and D8368 with no changes in hardware or setup.