AUTOMATED PIONA CLASS AND MULTI-PARAMETER ANALYSIS USING GC-VUV AND ASTM D8071

Application Benefits

- Provides both qualitative and quantitative analysis of hydrocarbon group type and select speciated hydrocarbon and oxygenate compounds.
- Better precision, repeatability, reproducibility, and accuracy compared to alternative approaches.
- EPA equivalence for ASTM D5769 (aromatics & benzene), ASTM D1319 (aromatics & olefins), ASTM D3606 (benzene), and ASTM D5599 (ethanol).
- Approved alternative to CGSB 14.3 for aromatic, olefin, ethanol, and benzene determination.
- Approved alternative to ASTM D6550 for olefin determination by the California Air Resources Board (CARB).
- No sample preparation, calibration curves, or deuterated internal standards.
- Rapidly separate and quantify key species and classes of compounds (34-minute run time).
- Automated analysis and reporting using VUV Analyze™ Software.
- Fully compliant with ASTM D8071.
- Cost-per-analysis is 12 times lower than alternative approaches.

VUV Analytics Solutions

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

KEYWORDS

gasoline, vacuum ultraviolet spectroscopy, VUV, VGA, paraffins, isoparaffins, olefins, naphthenes, aromatics, D8071, D5769, D1319, D3606, D5599, D6550

INTRODUCTION

Bulk compositional measurement of hydrocarbon groups and individual compounds in gasoline is important for ensuring compliance with various regulations as well as for determining fuel quality and expected performance. Being a very complex mixture and challenging to analyze, multiple methods have been developed to measure several parameters of gasoline samples, such as aromatic, olefin, and ethanol content.

Traditional methods are limited in scope to a subset of hydrocarbon groups or specific compounds of interest, meaning that multiple methods are required to gather the necessary data to ensure compliance and quality. More comprehensive methods, such as ASTM D6730 and ASTM D6839, tend to involve complicated instrumentation and setup procedures. Table 1 summarizes several test methods and their respective scopes.

ASTM METHOD	D6550	D4815	D5599	D1319	D3606	D5769	D5580	D6729 / D6730	D6839	D8071
TECHNIQUE	SFC	MDGC-FID	GC-OFID	FIA	GC-TCD	GC-MS	MDGC-FID	GC-FID	Reformu-lyzer®	GC-VUV
Aromatics				✓		✓	✓	✓	✓	✓
Benzene					✓	✓	✓	✓	✓	✓
Olefins X	✓			✓				✓	✓	✓
Ethanol		✓	✓					✓	✓	✓
Ethyl Bz.						✓	✓	✓		✓
IsoParaffin								✓	✓	✓
Methanol		✓	✓					✓		✓
Methyl Naph.								✓		✓
Naphthalene								✓		✓
Naphthene								✓	✓	✓
Paraffin								✓	✓	✓
Toluene					✓	✓	✓	✓		✓

Table 1: Several gasoline test methods and their parameters.

This application note describes an approach to achieving PIONA class and multi-parameter analysis with a single measurement using the VUV Analyzer Platform for Fuels running ASTM D8071.

Experimental

GC Conditions

Injection Volume: 1μL
Inlet Temperature: 250°C
Split Ratio: 300:1
Column: 100% non-polar PDMS Column (30m x 0.25, 0.25 μm)
Carrier gas: Helium; 1mL/min
Oven Program: 35°C, hold 10 min; 7°C/min to 200°C, hold 0
Run Time: 33.6 minutes

VGA Conditions

Makeup Gas Pressure: N2
(pressure determined on instrument)
Flow Cell Temperature: 275°C
Transfer Line Temperature: 275°C
Acquisition Frequency: 4.5 Hz
Acquisition Range: 125 - 240 nm

RESULTS AND DISCUSSION

A simple five-step analytical workflow (Figure 1) is employed to determine carbon breakdown and compounds of interest in a variety of gasoline samples. The gasoline samples do not require any special sample preparation and are run on the 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 D8071.

1	**SYSTEM VALIDATION**	Chemical standards are 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 Gasoline Application for ASTM D8071.
5	**QUANTITATION**	Automated with VUV Analyze Software. Relative Response Factors > mass %. Densities > volume %.

Figure 1: Analytical workflow for GC-VUV gasoline analysis using ASTM D8071.

Traditional chromatography identifies and quantifies compounds using peak retention time and peak tables. Because of this, it is important that peaks of interest are sufficiently baseline resolved. As gasoline is a complex mixture of hydrocarbons, achieving sufficient baseline resolution can be difficult as numerous compounds tend to coelute. Using a longer column can provide better separation, but it will also extend run times. Alternatively, other techniques sometimes require the use of complex valves, multiple columns, and compound and class-specific traps. PIONA analysis using GC-VUV conversely leverages spectral validation. As a result, analysis of gasoline can be accomplished quickly using a single 30-meter column solution.

RESULTS AND DISCUSSION (cont.)

For this application, using the VUV Analyzer for Fuels, we acquired data for a reformulated gasoline sample that contains over 300 individual compounds -- VUV-CS. This sample was acquired using a 30-meter, non-polar PDMS column with a runtime of 34 minutes. Figure 2 shows the output chromatogram. While it is not obvious by looking at the chromatogram, there are several coeluting compounds that make it difficult to analyze using traditional retention time approaches.

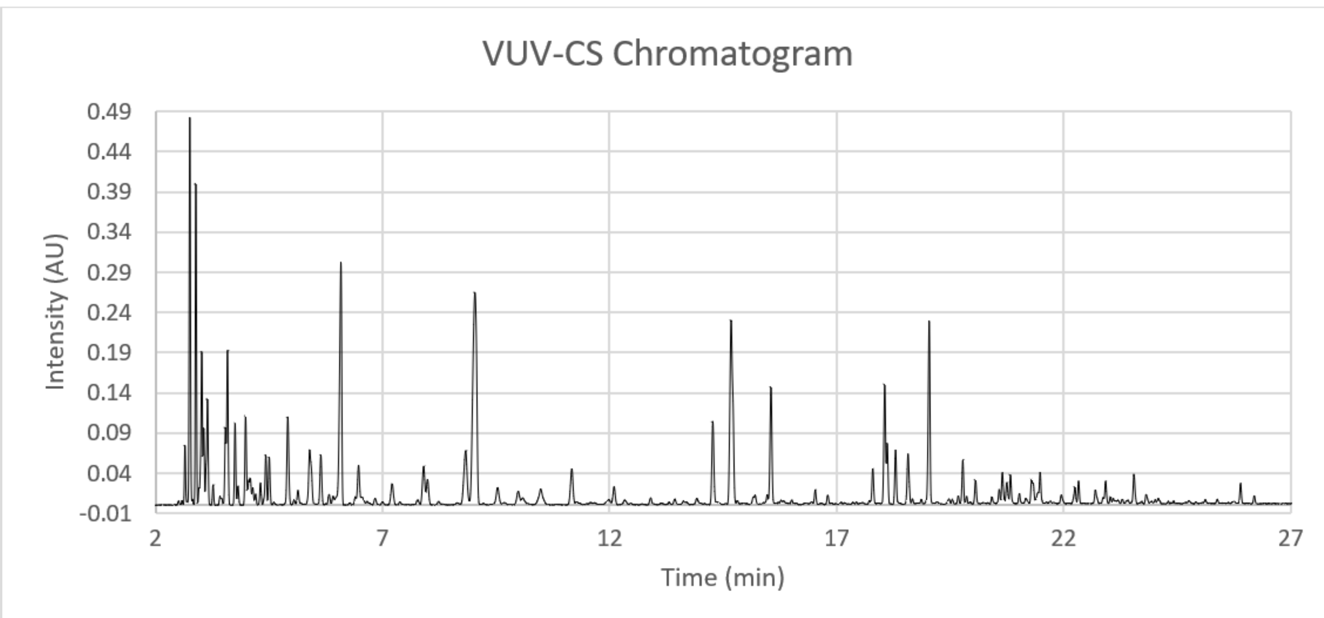


Figure 2: Reformulated gasoline sample with no spectral filters applied.

However, GC-VUV is a three-dimensional technique, where data is acquired on three axes – time, absorbance, and wavelength. As a result, each compound has a unique spectral shape. Additionally, the individual spectra from compounds in a given class share similar shapes. This is significant because the class-based spectra can be combined to provide accurate class-based analysis that is required for PIONA.

Figures 3 – 7 display the spectral filters associated with each of the PIONA classes along with an overlay of the individual spectra that are used in that filter. As you can see, spectra of a given class share similar shapes. Spectral filters give a good representation of where and when compounds of a given class absorb in the GC-VUV chromatogram.

RESULTS AND DISCUSSION (cont.)

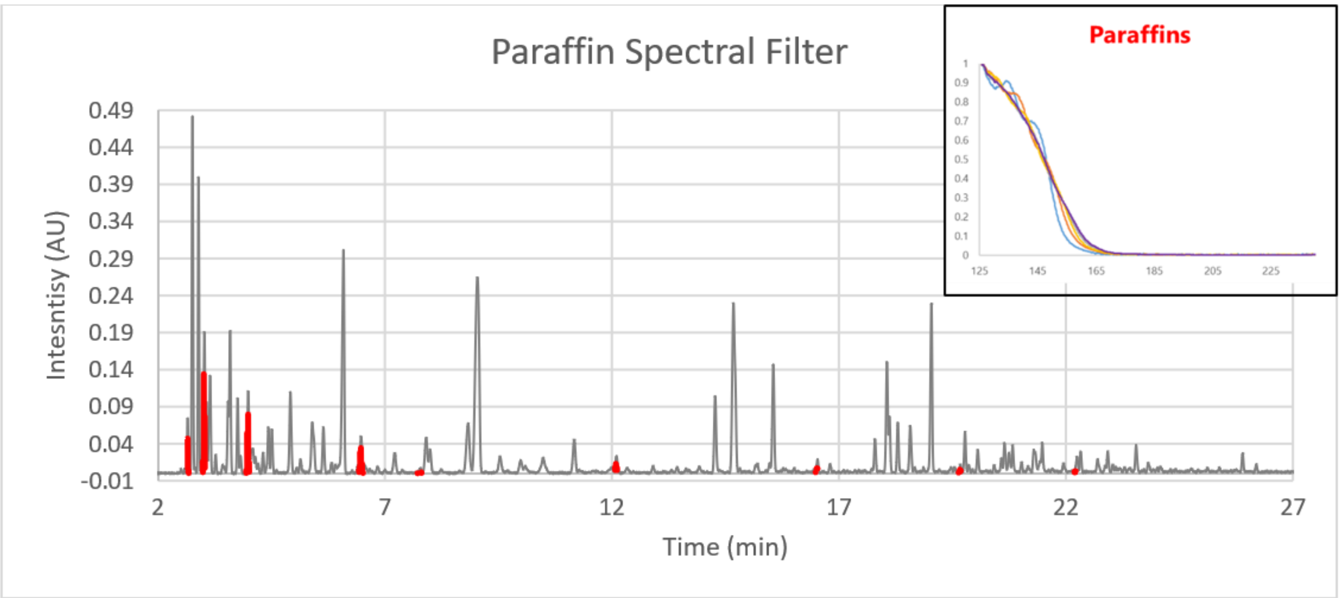


Figure 3: Reformulated gasoline chromatogram with paraffiin spectral filter applied. The inset shows the VUV absorbance spectra of several common parrafins.

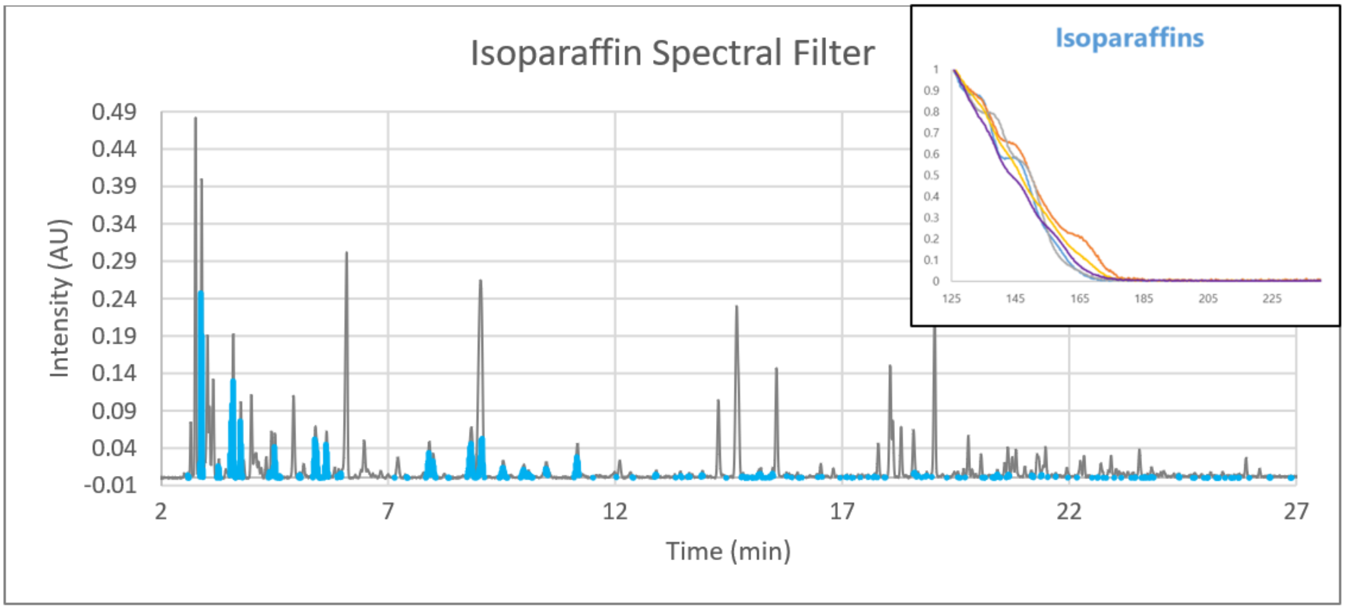


Figure 4: Reformulated gasoline chromatogram with isoparaffiin spectral filter applied. The inset shows the VUV absorbance spectra of several common isoparaffins.

RESULTS AND DISCUSSION (cont.)

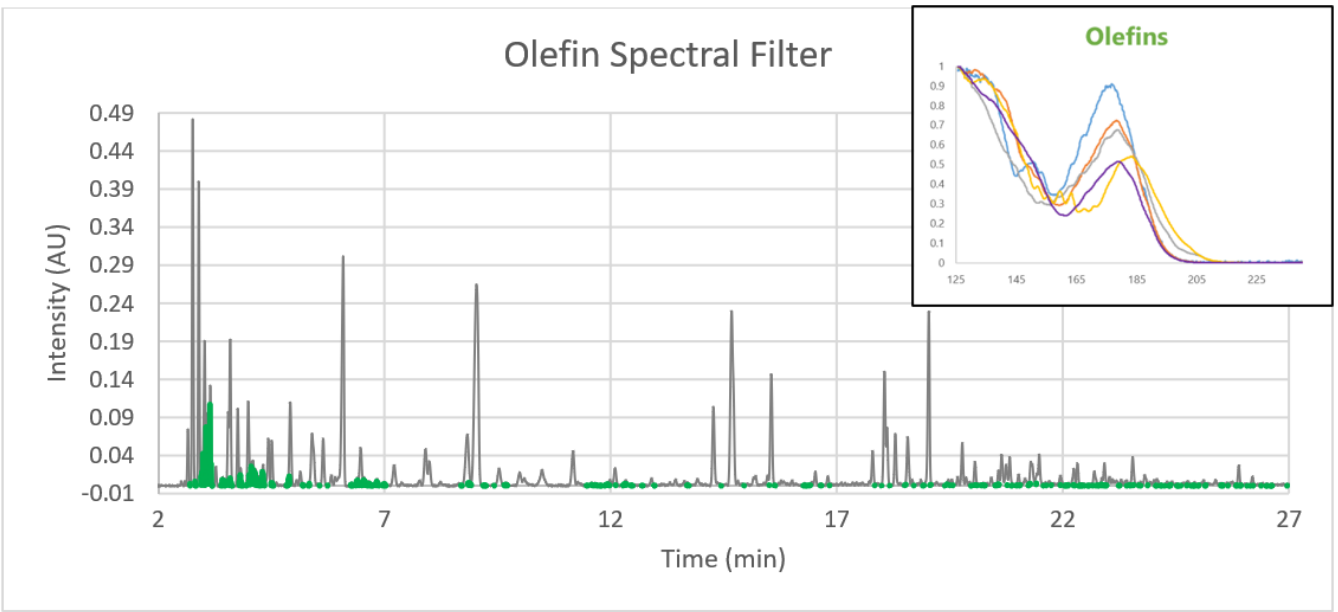


Figure 5: Reformulated gasoline chromatogram with olefin spectral filter applied. The inset shows the VUV absorbance spectra of several common olefins.

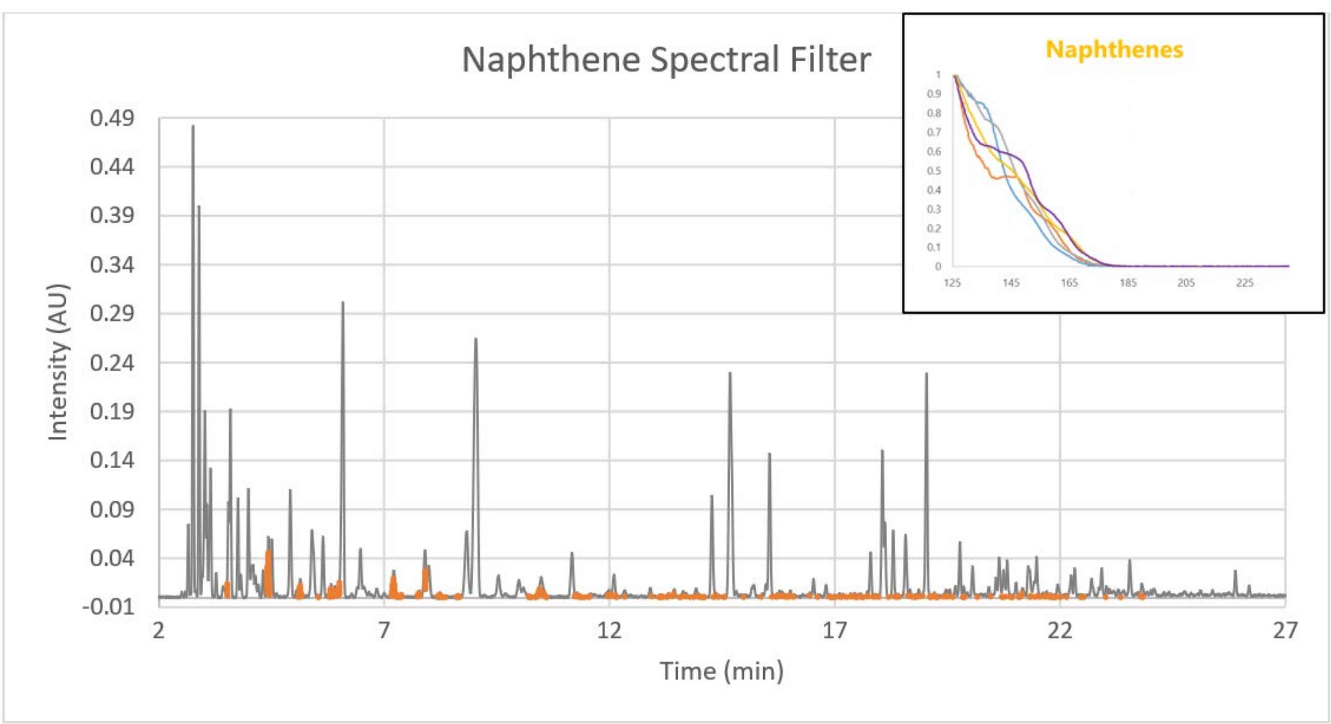


Figure 6: Reformulated gasoline chromatogram with naphthene spectral filter applied. The inset shows the VUV absorbance spectra of several common naphthenes.

RESULTS AND DISCUSSION (cont.)

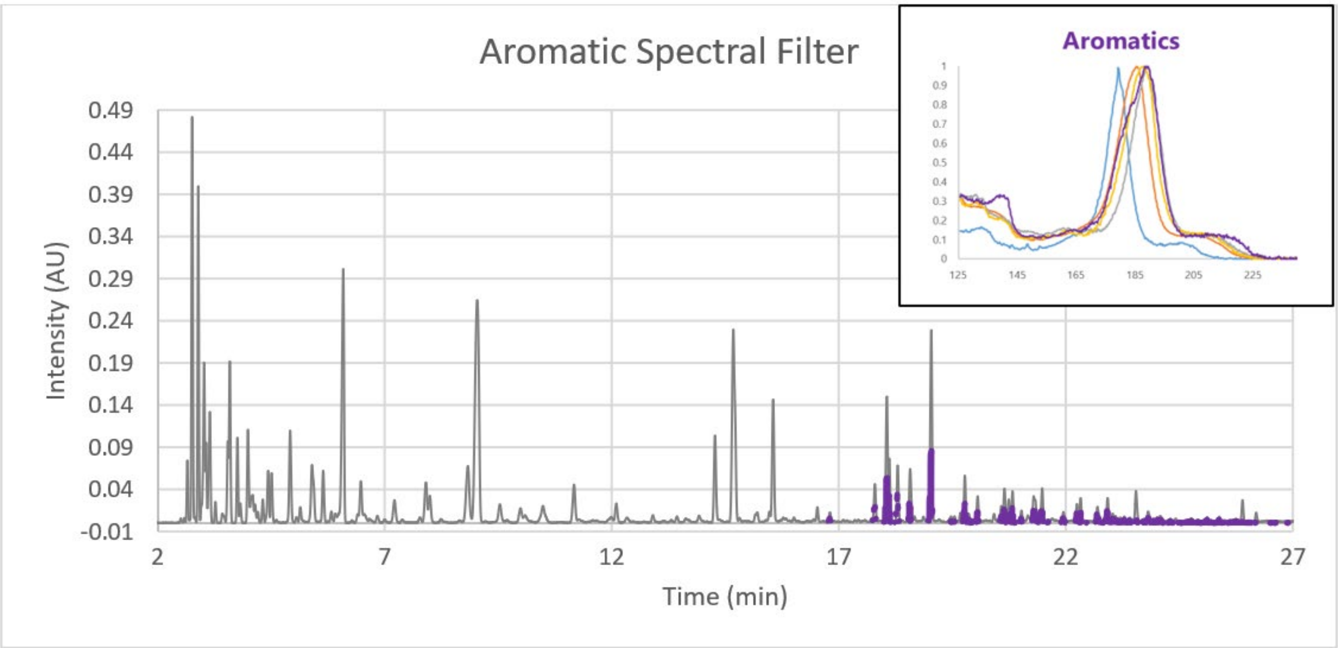


Figure 7: Reformulated gasoline chromatogram with aromatic spectral filter applied. The inset shows the VUV absorbance spectra of several common aromatic compounds.

CLASS-BASED DATA ANALYSIS

Reviewing figures 2 – 6, you will notice that several classes of compounds coelute in the GC-VUV chromatogram. However, with the VUV Analyzer Platform, the GC-VUV chromatogram is divided into regularly spaced time intervals during analysis. Each spectrum can then be automatically compared and matched against a compound library and analyzed to determine the contribution of each compound. This automated approach is called Time Interval Deconvolution™, and it allows for accurate class-based analysis. When a coelution occurs, VUV Analyze Software uses the unique spectral shapes of each class and compound to determine the best multi-analyte fit.

After VUV Analyze Software completes the carbon number and class categorization (described above) of the components within the sample, an automated calculation determines the mass percent and volume percent makeup. The result is a table based on compound class as seen in Table 2.

CLASS-BASED DATA ANALYSIS (cont.)

MASS %						
C. No.	P	I	O	N	A	Total
C1						
C2						
C3						
C4	1.1144	0.1064	0.0450			1.2657
C5	2.9113	6.0742	3.7817	0.2446		13.0118
C6	2.0138	6.9951	2.2886	1.6600	0.8034	13.7610
C7	1.2529	5.5536	0.8038	2.0491	3.8278	13.4871
C8	0.5290	17.2473	0.7076	2.0670	5.7730	26.3239
C9	0.3473	3.2496	0.1982	0.9024	5.9828	10.6802
C10	0.2080	0.8515	0.6075	0.9567	3.1507	5.7743
C11	0.1045	0.9554	0.3179	0.5486	1.3512	3.2776
C12		0.1992	0.1638	0.0571	0.3897	0.8098
C13		0.1849	0.0491		0.2292	0.4633
C14		0.0445				0.0445
C15		0.0028				0.0028
C16						
C17						
C18						
C19						
Total	8.4811	41.4645	8.9633	8.4855	21.5077	

VOLUME %						
C. No.	P	I	O	N	A	Total
C1						
C2						
C3						
C4	1.4101	0.1398	0.0538			1.6037
C5	3.4051	7.1802	4.1864	0.2404		15.0121
C6	2.2368	7.7921	2.3616	1.6090	0.6695	14.6690
C7	1.3422	5.9535	0.8039	1.9908	3.2336	13.3239
C8	0.5515	17.9972	0.7041	1.9749	4.8632	26.0909
C9	0.3545	3.3225	0.1979	0.8451	5.0351	9.7550
C10	0.2087	0.8459	0.5969	0.8663	2.6164	5.1341
C11	0.1034	0.9195	0.3101	0.4966	1.1072	2.9368
C12		0.1892	0.1581	0.0511	0.3162	0.7147
C13		0.1741	0.0469		0.1925	0.4135
C14		0.0416				0.0416
C15		0.0026				0.0026
C16						
C17						
C18						
C19						
Total	9.6122	44.5583	9.4195	8.0742	18.0337	

Table 2: ASTM D8071 results are presented in an easy-to-read table showing carbon number and class breakdown. Note that Ethanol is not included in the PIONA table above. As a result Totals only equal 88.9.

INDIVIDUAL COMPOUND SPECIATION

In addition to class-based reporting, the VUV Analyzer Platform running ASTM D8071 provides detailed insight into key compounds of interest. For fuels certification, those compounds include: methanol, ethanol, benzene, iso-octane, toluene, ethylbenzene, naphthalene, methylnaphthalenes, and xylenes (Table 3) – with the option to add others for non-regulated use.

Individual speciated compounds can be identified, even if they coelute, using Time Interval Deconvolution described above.

REPORT ITEM	CATEGORY	RETENTION TIME (min)	MASS%	VALUME %
Methanol	Alcohol	-	-	-
Ethanol	Alcohol	2.7468	11.0980	10.3021
Benzene	Aromatic	4.9224	0.8034	0.6695
iso-octane	Isoparaffin	6.0768	7.2400	7.6640
Toluene	Aromatic	9.0894	3.8278	3.2336
Ethylbenzene	Aromatic	14.2686	1.0800	0.9123
Naphthalene	Aromatic	23.5260	0.2053	0.1467
Methylnaphthelenes	Aromatic	-	0.2372	0.1725
Xylenes	Aromatic	-	4.6930	3.9508

Table 3: Individual speciated compounds identified in reformulated gasoline sample VUV-CS.

METHOD SCOPE AND COMPLIANCE REPORTING

MATRIX	PROPERTY	UNITS	MIN	MAX	REPLACES METHODS	APPROVALS
	Paraffins	% Volume	3.572	23.105		
	Isoparaffins	% Volume	22.697	71.993		
	Olefins	% Volume	0.011	44.002	ASTM D1319	
	Olefin	% Mass	0.027	41.954	ASTM D6550	
	Naphthenes	% Volume	0.606	18.416		
Gasoline	**Aromatics**	% Volume	14.743	58.124	ASTM D1319, ASTM D5769	EPA
E10	**Methanol**	% Volume	0.063	3.426		CARB
E15	**Ethanol**	% Mass	0.042	15.991	ASTM D5599	CGSB
	Benzene	% Volume	0.09	1.091	ASTM D5769, ASTM D3606	
	Toluene	% Volume	0.698	31.377		
	Ethylbenzene	% Volume	0.5	3.175		
	Xylenes	% Volume	3.037	18.955		
	Naphthalene	% Volume	0.019	0.779		
	Methylnaphthalenes	% Volume	0.21	1.484		

Table 4: ASTM D8071 scope.

ASTM D6708 studies have been conducted to determine correlation between ASTM D8071 and ASTM methods D1319 (aromatics and olefins), D3606 (benzene), D5769 (aromatics and benzene), and D5599 (ethanol), and are recognized by the U.S. Environmental Protection Agency (EPA) as suitable alternatives. Correlation with CGSB 14.3 for benzene measurement has also been determined and is an accepted alternative by the Canadian General Standards Board, as well as correlation with ASTM D6550 as per the California Air Resources Board.

The applicable ASTM D8071 test result range for ASTM D6708 correlation equations are shown in Table 5:

		ASTM D8071 Reported Results		
CORRELATED METHOD	**UNITS**	**MIN**	**MAX**	**CORRELATION EQUATION**
ASTM D1319 (aromatics)	% Volume	14.743	58.124	(D8071 vol%) - 0.8313
ASTM D1319 (olefins)	% Volume	0.0190	17.412	(D8071 vol%)*0.827 + 0.5318
ASTM D3606 (benzene)	% Volume	0.12	0.946	(D8071 vol%)*0.968 - 0.016
ASTM D5599 (ethanol)	Mass %	0.396	15.991	(D8071 mass%) - 0.0878
ASTM D5769 (aromatics)	% Volume	14.743	36.068	(D8071 vol%) - 1.097
ASTM D5769 (benzene)	% Volume	0.09	1.09	(D8071 vol%)*0.9446 - 0.0014
ASTM D6550 (olefins)	Mass %	0.24	16.71	(D8071 mass%) + 0.2979

Table 5: The applicable test ranges for ASTM D6708 correlation equations.

Results for the ASTM D6708 correlations are automatically generated based on the above ranges and output separately on your report in a section called ASTM D6708 Predicted Values.

REPEATABILITY AND REPRODUCIBILITY

Precision for the VUV Analyzer for Fuels running ASTM D8071 was determined by an interlaboratory study (ILS) that included 21 laboratories and 27 fuel samples. This ILS included a variety of gasoline sample types including FCC gasoline, European petrol, Canadian gasoline, USA conventional gasoline, USA reformulated gasoline, and others. Supporting data for this ILS may be obtained from ASTM by requesting Research Report RR:1909.

The repeatability (r) and reproducibility (R) of ASTM D8071 as compared to the established ASTM referee methods is summarized in Figures 8 and 9 respectively. As indicated in the figure, ASTM D8071 has been demonstrated to have up to ~3 times better repeatability and ~4 times better reproducibility than the alternative methods.

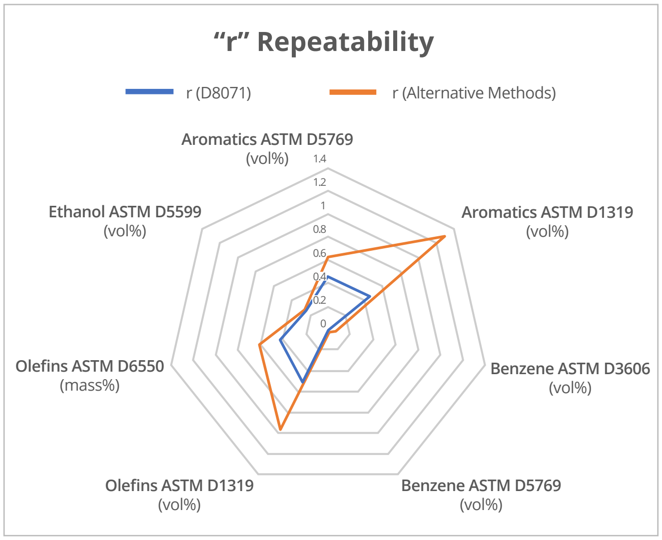


Figure 8: Comparison of method repeatability.

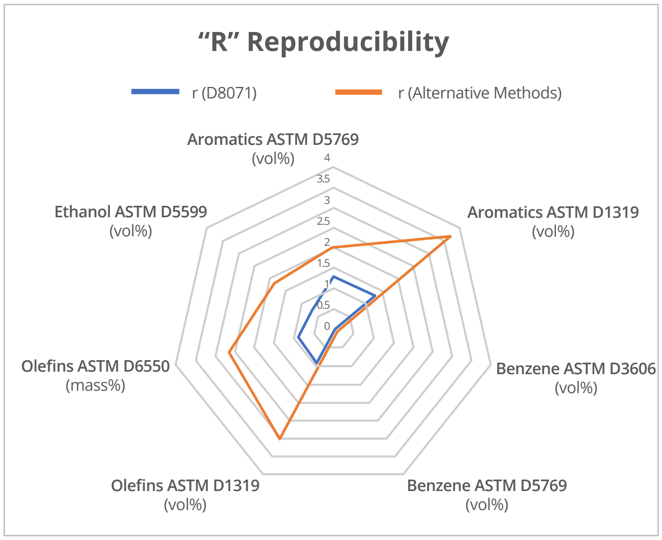


Figure 9: Comparison of method reproducibility.

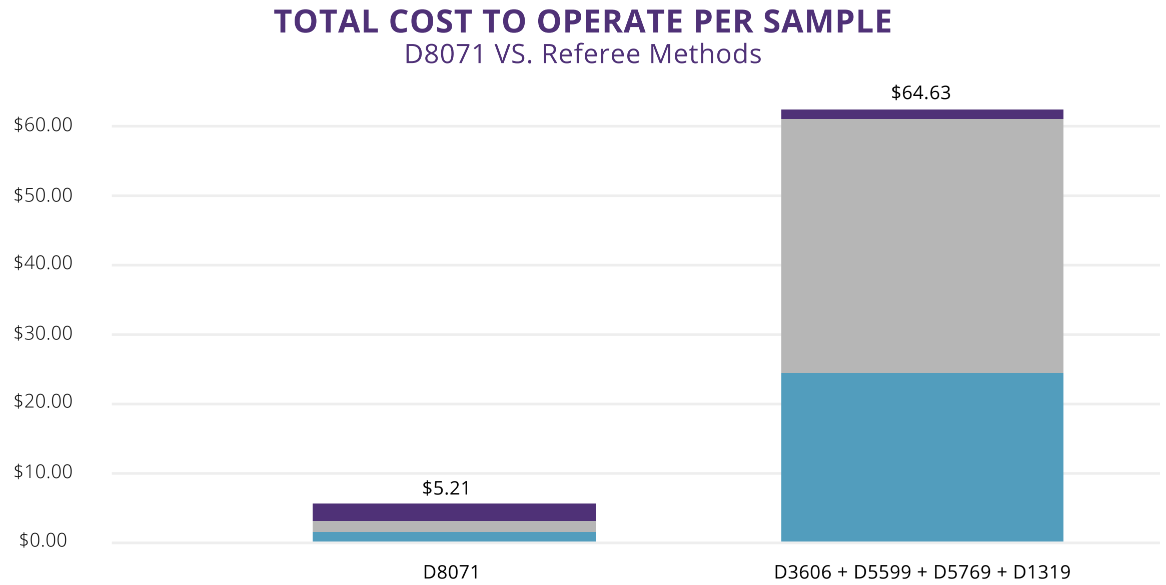
COST PER ANALYSIS

Cost-per-analysis using GC-VUV running ASTM D8071 is significantly less on a per-sample basis than the alternative approaches. This is due in large part to lower labor and consumables costs resulting from the elimination of sample preparation and complex apparatus setup, automation provided by the VUV Analyze Software, minimal ongoing consumable and maintenance costs, and the consolidation of multiple techniques into a single, easy-to-use method.

To better compare cost-per-analysis, ASTM D8071 was compared to ASTM D1319, ASTM D3606, ASTM D5599, and ASTM D5769, each of which ASTM D8071 has ASTM D6708 equivalency with. To ensure 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 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 substantial difference in cost-per-analysis between ASTM D8071 and the alternative methodologies required to acquire the same data set. While having similar capital costs, the consumables and labor costs when using ASTM D8071 are over 12 times less expensive to run on a per-sample basis than compared to the alternative methodologies.

COST PER ANALYSIS (cont)



	D8071	D3606 + D5599 + D5769 + D1319
Capitol	$2.63	$3.31
Labor	$1.42	$36.33
Consumables	$1.16	$24.98
Total Cost / Sample	$5.21	$64.63

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 D8071 determines hydrocarbon group types and select hydrocarbon and oxygenate compounds in gasoline with significantly better precision, repeatability (r) and reproducibility (R) than the alternatives – TCD (ASTM D3606), OFID (ASTM D5599), GC/MS (ASTM D5769), and FIA (ASTM D1319).

Gasoline analysis using the VUV Analyzer for Fuels is fast. Acquisition and analysis takes only 34 minutes.

Gasoline analysis is significantly easier using the VUV Analyzer Platform for Fuels running D8071 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 Platform for Fuels and ASTM D8071 is 12 times less expensive to run on a per-sample basis compared to the alternative methodologies.