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Automated, multi-parameter gasoline characterization using GC-VUV and ASTM D8071

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Keywords

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Goal

This application note details an innovative method for fully automated PIONA class analysis and hydrocarbon profiling of gasoline using gas chromatography with vacuum ultraviolet detection (GC-VUV) under ASTM D8071.[1] The method delivers comprehensive compositional data—including paraffins, isoparaffins, olefins, naphthenes, aromatics, ethanol, and benzene—in a single 34-minute run. With no sample prep, calibration standards, or multiple instruments required, this platform significantly reduces cost-per-sample and complexity, while improving precision and compliance with global fuel regulations.

Introduction

Gasoline is a complex hydrocarbon blend whose composition directly impacts combustion behavior, emissions, and regulatory compliance. Accurately quantifying components such as aromatics, olefins, ethanol, and benzene is critical, but traditional ASTM methods require multiple techniques (FIA, GC-FID, GC-MS, etc.) to measure all relevant parameters. Table 1 summarizes several test methods and their respective scopes.

ASTM D8071 introduces a consolidated method using GC-VUV, offering improved precision, spectral resolution, and reduced operational burden. This approach is now recognized as an EPA- and CARB-approved alternative to several legacy test methods, including ASTM D1319, D5599, D5769, and D3606.

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Table 1. Several gasoline test methods and their parameters

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	Reformulyzer™	GC-VUV
Aromatics				✓		✓	✓	✓	✓	✓
Benzene					✓	✓	✓	✓	✓	✓
Olefins	✓			✓				✓	✓	✓
Ethanol		✓	✓					✓	✓	✓
Ethyl Benzene						✓	✓	✓		✓
Isoparaffin								✓	✓	✓
Methanol		✓	✓					✓		✓
Methyl Naphthalene								✓		✓
Naphthalene								✓		✓
Naphthene								✓	✓	✓
Paraffin								✓	✓	✓
Toluene					✓	✓	✓	✓		✓

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.[2]

Experimental

Gasoline samples were analyzed on the VUV Analyzer Platform for Fuels with no sample preparation required. The VUV Analyzer consists of the Thermo Scientific™ TRACE™ 1610 gas chromatograph coupled to the VGA-100™ spectrometer detector (VUV Analytics, Inc.).

Data are acquired and processed with the VUVision™ Software and VUV Analyze™ Software (VUV Analytics, Inc), respectively, specifically configured to run ASTM D8071.

Workflow overview

The VUV Analyzer Platform for Fuels performs gasoline PIONA class analysis using a streamlined five-step workflow:

1. **System validation** – Verifies instrument performance using standard hydrocarbons.
2. **Sample prep** – No preparation required.
3. **Data acquisition** – Performed using VUVision Software.
4. **Spectral matching** – Automated deconvolution with VUV Analyze Software.
5. **Quantitation** – Volume % and mass % calculated with high accuracy using built-in response factors and density data.

Results and discussion

Three-dimensional spectral analysis

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.

Unlike conventional GC, GC-VUV collects data across three axes: retention time, absorbance, and wavelength. Every compound has a unique spectral fingerprint, and members of the same hydrocarbon class (e.g., aromatics or olefins) exhibit similar absorbance patterns. This spectral distinction allows for accurate class separation even in the presence of coelution. As a result, analysis of gasoline can be accomplished quickly using a single 30-meter column solution.

Reformulated gasoline samples containing over 300 compounds were analyzed using a single-column setup in just 34 minutes, as shown in Figure 1.

Class-specific spectral filters are applied to overlay the chromatogram and distinguish paraffins, isoparaffins, olefins, naphthenes, and aromatics visually and analytically. Class-based spectra can be combined to provide accurate class-based analysis that is required for PIONA.

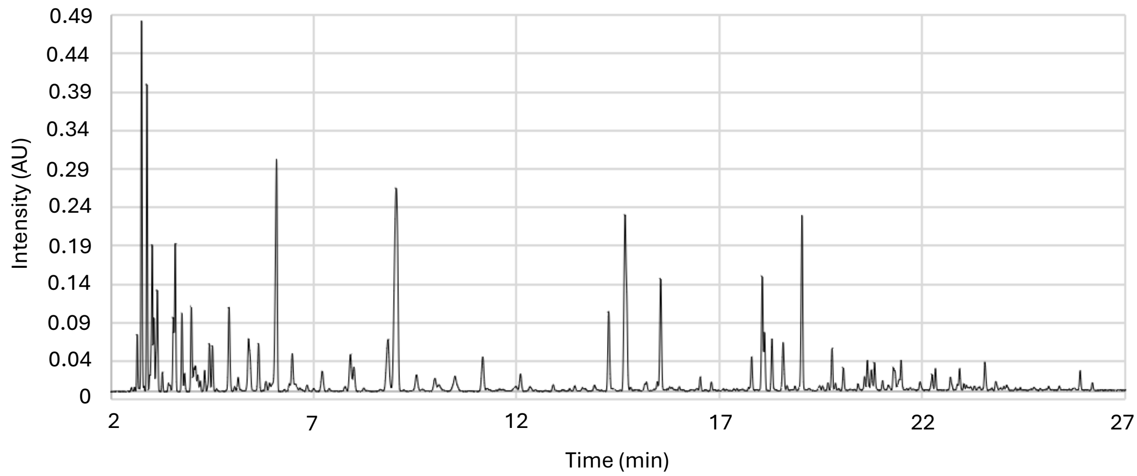


Figure 1. Reformulated gasoline sample with no spectral filters applied

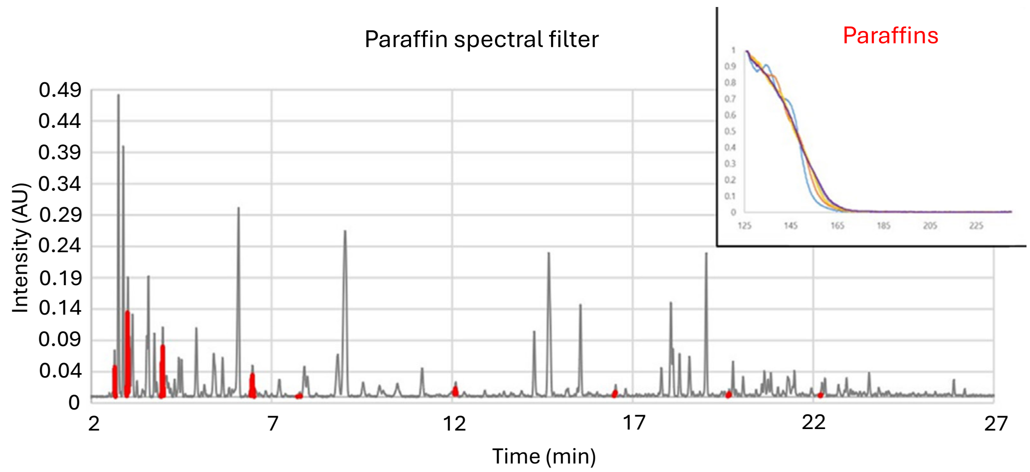


Figure 2. Reformulated gasoline chromatogram with paraffin spectral filter applied. The inset shows the VUV absorbance spectra of several common paraffins.

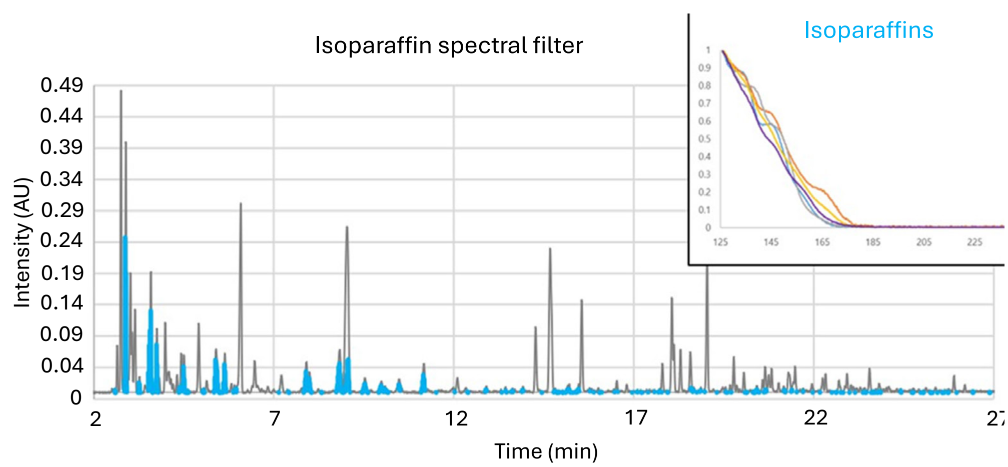


Figure 3. Reformulated gasoline chromatogram with isoparaffin spectral filter applied. The inset shows the VUV absorbance spectra of several common isoparaffins.

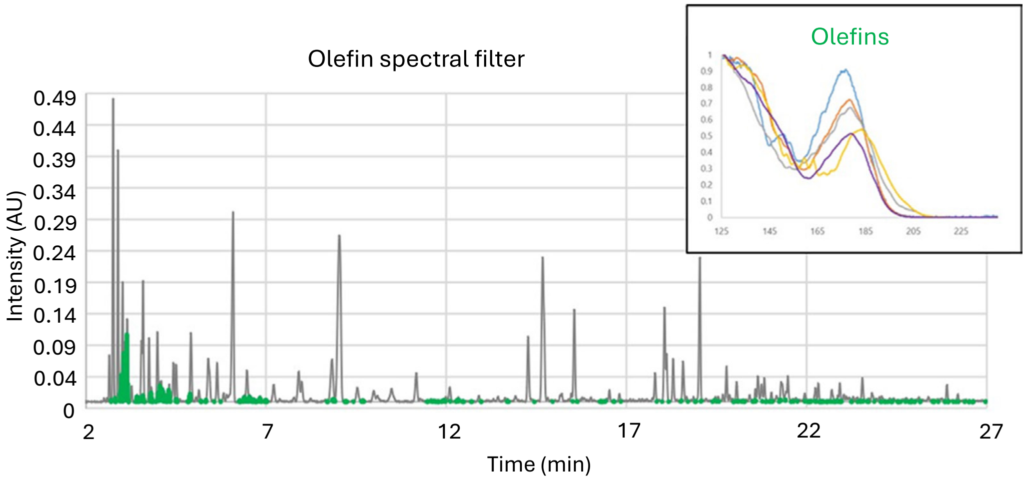


Figure 4. Reformulated gasoline chromatogram with olefin spectral filter applied. The inset shows the VUV absorbance spectra of several common olefins.

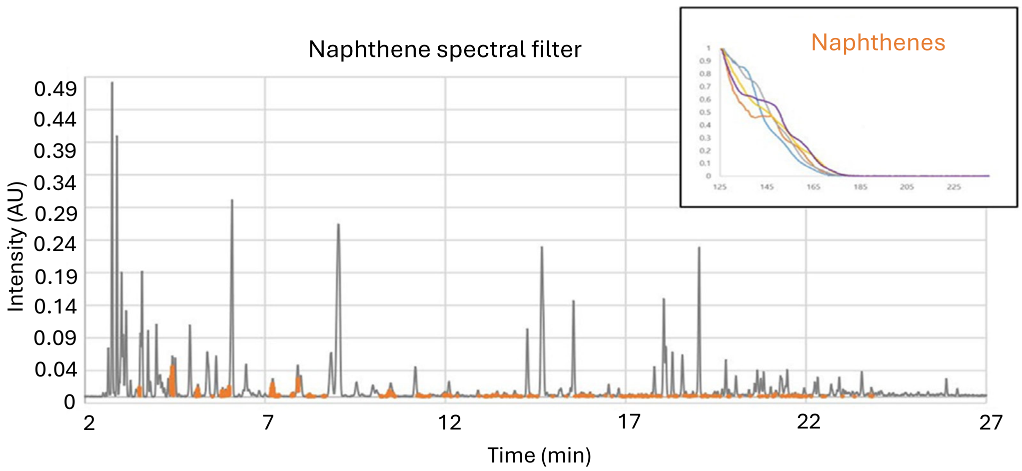


Figure 5. Reformulated gasoline chromatogram with naphthene spectral filter applied. The inset shows the VUV absorbance spectra of several common naphthenes.

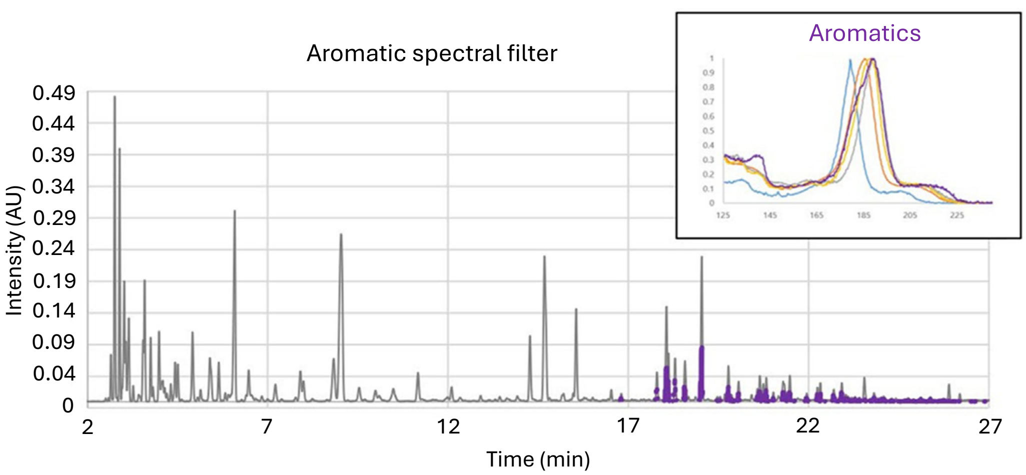


Figure 6. Reformulated gasoline chromatogram with aromatic spectral filter applied. The inset shows the VUV absorbance spectra of several common aromatics.

Figures 2–6 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 one 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.

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 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 (Table 2).

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, methylnaphthalene, and xylenes (Table 3), with the option to add other compounds for non-regulated purposes. Individual speciated components can be identified, even if they coelute, using the Time Interval Deconvolution described above.

Key outcomes

- Accurate quantification of PIONA classes with coelution resolved via spectral deconvolution
- Ethanol, benzene, toluene, xylenes, and other regulatory targets detected and quantified
- Results presented as both volume % and mass % across carbon number
- Easy-to-read tables and overlays simplify data interpretation

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. As a result, totals equal only 88.9.

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		13.011
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				0.044
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	0.714
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 3. Individual speciated compounds identified in reformulated gasoline sample

Report item	Category	Retention time (min)	Mass%	Volume %
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 4. The applicable test ranges for ASTM D6708 correlation equations

		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%) x 0.827 + 0.5318
ASTM D3606 (benzene)	% Volume	0.12	0.946	(D8071 vol%) x 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%) x 0.9446 - 0.0014
ASTM D6550 (olefins)	Mass %	0.24	16.71	(D8071 mass%) + 0.2979

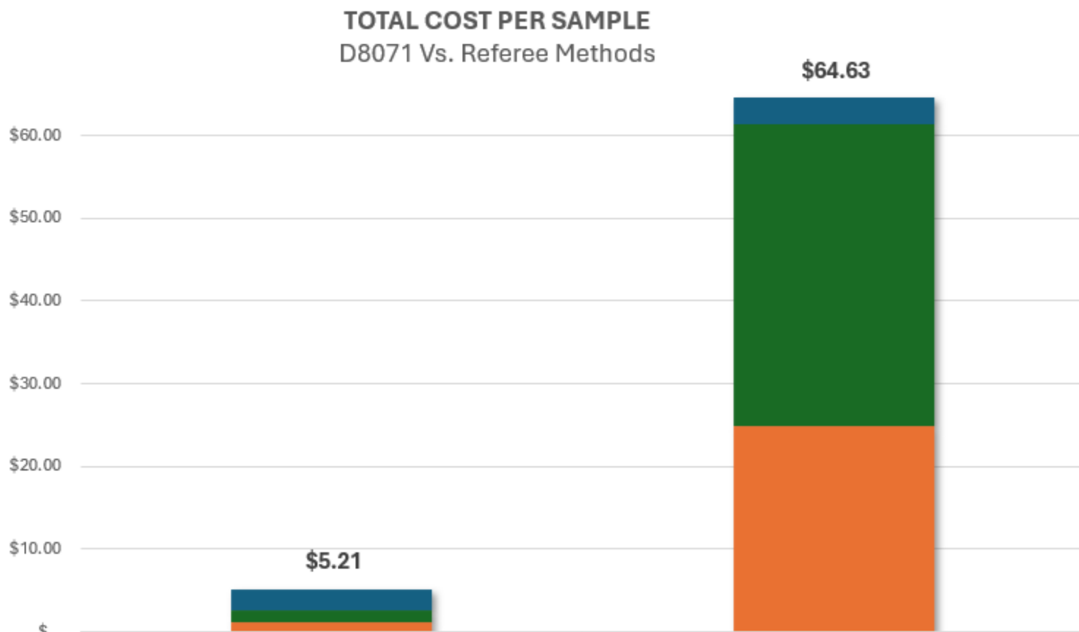
The applicable ASTM D8071 test result range for ASTM D6708 correlation equations, as shown in Table 4, provide equivalence to traditional referee methods. Regulatory agencies, including the EPA, CGSB, and CARB, have accepted this method as an alternative for multiple compound classes.

Cost advantages

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 7 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 compared to the alternative methodologies.



	D8071	D3606* + D5599* + D5769* + D1319*
Capital	$2.63	$3.31
Labor	$1.42	$36.33
Consumables	$1.16	$24.98
Total cost/sample	$5.21	$64.63

Consumables   Labor   Capital   Total cost/sample

Figure 7. Cost-per-sample analysis. Note that all values are in USD.

Conclusion

GC-VUV with ASTM D8071 enables complete hydrocarbon group and compound-level analysis of gasoline in a single method. Its ability to automate spectral deconvolution and report mass and volume percentages simplifies operations while meeting strict compliance standards. This solution not only enhances analytical accuracy and repeatability but also drastically reduces operating costs and lab complexity.

- Short analysis time with full gasoline class and compound profiling in 34 minutes
- Faster throughput with full automation from injection to reporting
- 12× lower cost-per-analysis, due to reduced labor, no calibration standards, and consolidated workflow

References

1. ASTM International - D8071 Standard Test Method
2. VUV Analytics – ASTM D8071 for Gasoline Analysis

Learn more at **thermofisher.com/gc-vuv**