

# Automated PIONA Analysis by ASTM D8071 and VUV PIONA+

## An Application of VUV PIONA+ for Finished Gasoline Analysis

### Introduction

ASTM D8071 is a single column, single injection method that provides complete compound class characterization of paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) in finished gasoline samples by Gas Chromatography and Vacuum Ultraviolet Spectroscopy (GC-VUV). Approved by ASTM D02 as "Standard Test Method for the Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)," the method uses straightforward instrumentation and does not require pre-column tuning or valve timing adjustments. ASTM D8071 is a production-worthy method with a 34-minute run time and rapid data analysis automation enabled by the VUV PIONA+ product solution.

VUV PIONA+ combines a VGA-100 vacuum ultraviolet (VUV) absorption gas chromatography (GC) detector and a data analysis engine called VUV Analyze™ that performs rapid spectral identification and quantitative analysis. GC-VUV absorbance data is three dimensional (retention time, VUV absorbance, and wavelength). VUV absorbance spectra are typically highly structured and distinct for individual chemical compounds, yet exhibit the intuitive property of having similar features when measuring related compound classes. VUV Analyze™ software implements equations and fit procedures that result in the deconvolution of co-eluting peaks and accurate reporting of individual compounds and bulk hydrocarbons in mass or volume percent. PIONA hydrocarbon compounds can be speciated up to C6 and characterized by bulk compound class analysis

at higher carbon numbers. In addition, specific analytes throughout the chromatogram such as aromatics belonging to the BTEX complex can be targeted for speciation. VUV PIONA+ is fully compliant with ASTM D8071.

Bulk compositional measurement of hydrocarbon groups and individual compounds in gasoline is important for quality control, as well as for ensuring compliance with various governmental regulations. As such, multiple ASTM methods exist for measuring various aspects of gasoline samples. Most of the methods are limited in scope to a subset of hydrocarbon groups or specific compounds of interest, meaning that multiple methods are required for typical production control. More comprehensive methods such as ASTM D6730 and ASTM D6839 tend to involve complicated instrumentation and/or setup procedures. These methods have no inherent ability for self-monitoring of measurement results (e.g., fit criteria or similar), and instead rely on precise definition and control of retention times, resulting in more error-prone production measurements.

ASTM D8071 via VUV PIONA+ provides PIONA compound class analysis in a single measurement. ASTM D8071 provides a per-measurement data set that would typically require the implementation of multiple ASTM methods (e.g. D5769, D5580, D1319, D6550, D3606, D4815, D5599, D5845). Verifying compound identity through VUV spectral identification and utilizing VUV Analyze™ automated data processing results in a method that



is more scalable from R&D to Production than alternative ASTM methods for gasoline analysis.

ASTM D8071 method uses relatively simple instrumentation: a gas chromatograph, a standard 30m nonpolar column, and a VGA-100 or VGA-101 VUV detector. Bulk concentrations of PIONA compounds are determined using the VUV Analyze™ data processing procedure that averages 1 – 2 minutes per sample. The software includes a database library of VUV reference spectra, compound class information, density, retention index values, relative response factors for each hydrocarbon class, as well as relative response factors for individually speciated compounds.

Fast GC method run times can be used given that VUV Analyze™ readily deconvolves co-elution among various species and hydrocarbon classes. The ASTM D8071 GC run can be completed in approximately 34 minutes. To provide a more advanced means for deconvolution of complex mixtures, a time interval deconvolution (TID) algorithm was created.

This algorithm allows the deconvolution of co-eluting compounds in an automated fashion. The GC-VUV chromatographic data set is divided into time interval slices that are analyzed individually using a general linear least squares regression procedure to transform the chromatogram into distinct responses from individual analytes or classes of analytes. Initially, a library of gasoline-range hydrocarbon and oxygenate spectra was recorded in the VUV spectral library containing molecular mass, chemical formula, and retention index fields. After acquisition of data for real samples, TID was used to rapidly segregate a large number of overlapping constituents in the chromatogram. After all time intervals had been analyzed, the total responses for the PIONA classes and each of the designated compounds to be speciated (e.g., benzene, toluene, and ethanol) were converted to percent mass contributions to the entire sample.

## Experimental

### ➤ Instrumentation and Standards

GC analysis was completed with the following setup:

**Detector:** VUV Analytics VGA-100

**Gas Chromatograph:** Agilent 6890 equipped with a 7683 model autosampler

**Column:** 30m x 0.25mm x 0.25µm Rxi-1ms

A PIONA standard kit was used to create the initial library. Thirteen ASTM gasoline proficiency samples were obtained from stock drawn from various US refineries. Representative gasoline samples were obtained to demonstrate the capabilities of ASTM D8071 via VUV PIONA+ described in Figures 1 and 2, as well as Table 1.

### ➤ Relative Mass Calculation

The VUV Analyze™ engine implements equations and fit procedures that result in deconvolution of absorbance spectra that contain contributions from multiple species. Since absorption is additive, overlapping peaks give a spectrum that corresponds to the sum of absorbance of each compound.

By knowing the compounds' cross sections, it is possible to determine the individual contribution of each compound using the following equation:

$$A(\lambda) = l \sum_{j=1}^N \epsilon_j(\lambda) c_j \quad (1)$$

where  $\lambda$  is the wavelength, and  $\epsilon$  is the molar extinction coefficient, which is directly related to the absorption cross-section via the Avogadro constant. This equation can be simplified by using the compounds' reference absorbance spectra ( $A^{ref}$ ) and determining their relative contributions to the absorbance signal via:

$$A(\lambda) = \sum_{j=1}^N f_j \times A_j^{ref}(\lambda) \quad (2)$$

Within each time slice, Equation 2 is used in conjunction with a tiered library search to determine the compound identities and/or classes that elute within the time slice, as well as their contributions to the total response. In most cases, the response is added to the corresponding class response. For compounds selected for speciation, their contributions are instead added to compound-specific totals.

The data processing includes a database library of VUV reference spectra, compound class information, density, approximate retention index values, relative response factors for each hydrocarbon class and relative response factors for individually reported compounds.

The compound class or specific compound concentrations can be reported as mass or volume percent:

$$M_a = 100 \times \frac{A_a \times RRF_a}{\sum_{i=1}^n A_i \times RRF_i} \quad (3)$$

where RRF is the relative response factor. In this work, the RRFs determined were relative to methane, which was assigned a RRF value of 1. Once a RRF for a compound is assigned, the RRF for any other compound can be determined when relative amounts of each are known by:

$$\frac{RRF_2}{RRF_1} = \frac{M_2}{M_1} \frac{A_1}{A_2} \quad (4)$$

where  $M_2/M_1$  is the relative mass of the two analytes, and  $A_1/A_2$  is the ratio of their measured response areas.

## Results and Discussion

Figure 1 shows a gasoline sample chromatogram where the PIONA compounds have eluted primarily between 1.5 and 25 minutes using the 30-meter nonpolar phase capillary GC column and conditions described by ASTM D8071. Spectral filters can be used as a visualization tool to assist in discriminating between different compound classes. In this work, spectral filters of 125 – 160 nm, 140 – 160 nm, and 200 – 240 nm were applied post-data acquisition to enhance analyte sensitivity in the region of interest. The inset figure shows a zoomed-in retention window of the early portion of the chromatogram. Very few of the peaks displayed have achieved baseline resolution, yet all of the corresponding compound classes can be distinctly identified and quantitated. Furthermore, the VUV Analyze™ software has identified each peak by its compound class (or classes) and color coded them appropriately. The same method conditions used in conjunction with a 60-meter column enables individual compounds to be chemically speciated up to C6, along with being grouped by class.

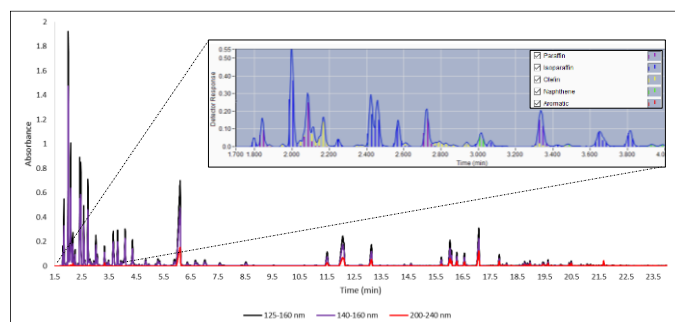


Figure 1: Gas chromatogram of gasoline sample. Inset figure shows zoomed-in retention window with high concentration of PIONA compounds.

Key chromatographic peaks representing Paraffin, Isoparaffin, Olefin, and Naphthene compounds in the 1.5 – 4.5 minute retention time window are labelled in Figure 2. The VUV Analyze™ software can rapidly identify these compound classes based on their distinct spectral characteristics and provide quantitative values of compounds detected within each class. This PIONA compound class analysis is automated to provide rapid identification and quantitation of chromatogram peaks. Figure 2 inset shows the VUV absorbance spectrum and fit of an olefin compound between 2.0 and 2.2 minutes. VUV Verified™ analyte identification is accomplished by rapidly comparing analyte absorbance data to the known spectral profiles of PIONA compounds. The analyte in Figure 2 is identified as being an olefin compound and verified by the overlapping fit spectrum. The zero-value residual fit data further validates the olefin compound class identity. VUV PIONA+ eliminates the error inherent to alternative detection technologies that rely on retention time position for compound/class identification.

quantitated along with the PIONA characterization. An additional small proportion of PAHs was also quantitated and reported separately. PIONA-specific reports with these quantitative parameters can be easily automated using the VUV Analyze™ software.

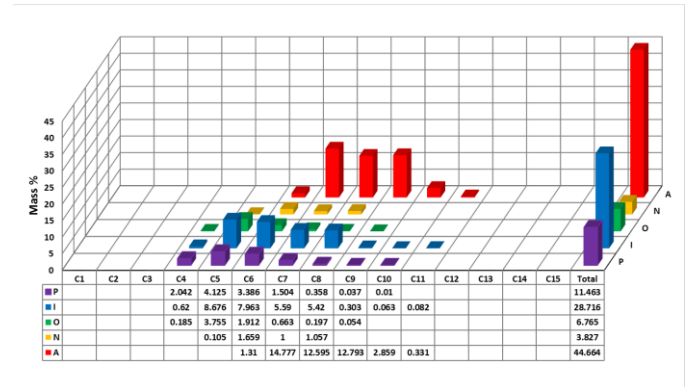


Table 1: Carbon number and mass % composition of the PIONA compounds featured in Fig 1 and 2.

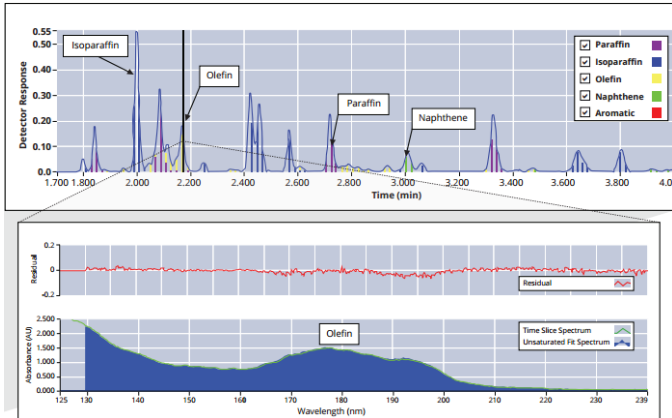


Figure 2: Zoomed-in chromatogram of gasoline sample with key PIONA compound class representative peaks labeled. Inset figure shows olefin spectral and residual fit data.

Table 1 displays the carbon number and mass % composition of the PIONA compounds featured in Fig 1 and 2. The VUV Analyze™ report provides the carbon number breakdown within each PIONA compound class, as well as the mass or volume percent of PIONA classes relative to each other. Not shown in the table is a small proportion of oxygenates (~4%) that were identified and

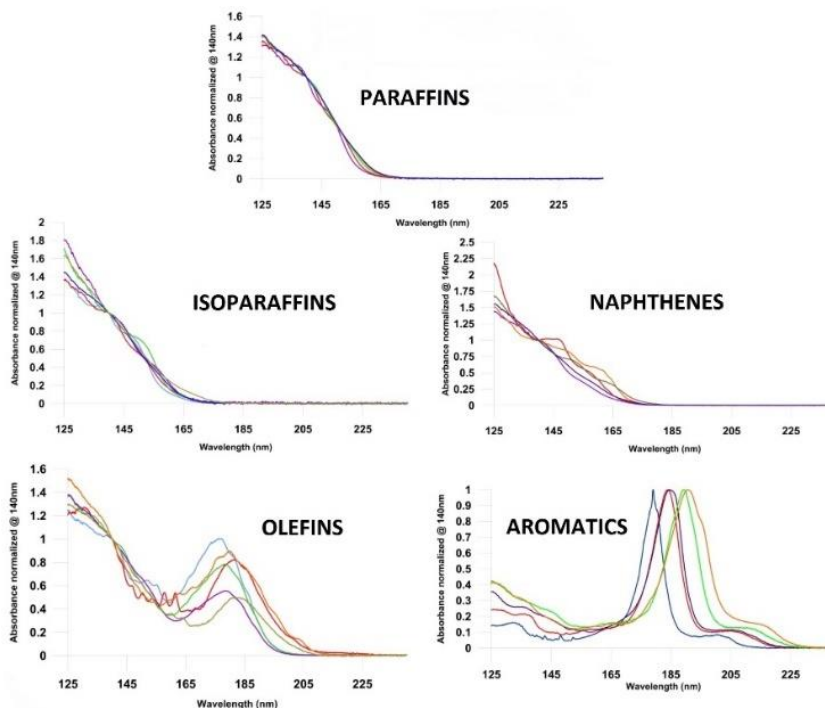


Figure 3: VUV absorbance spectra of PIONA compounds. Each compound class displays distinct spectral features, yet spectra within each category are distinct and lead to individual compound speciation.

Figure 3 demonstrates the detection capabilities inherent to VUV absorbance spectroscopy and exploited by VUV PIONA+. Each PIONA compound class has distinct spectral characteristics, yet individual compounds within a class can be identified and quantitated due to their unique absorbance cross sections. These sometimes-subtle spectral differences between compound class components make it possible to unambiguously identify and quantitate co-eluting analytes or classes within complex mixtures.

ASTM D8071 was applied to 13 ASTM proficiency samples (Table 2). The total time of the GC method run was approximately 34 minutes, although all compounds of interest were typically eluted within 30 minutes. Each measurement simultaneously determined bulk mass % values of paraffin, isoparaffin, olefin, naphthene, and aromatic classes, along with the individual speciation of ethanol, iso-octane, benzene, toluene, ethylbenzene, total xylene, naphthalene, and total methylnaphthalene. Table 2 shows the range of values for these parameters over the entire 13 sample set, illustrating the range of process variation covered by ASTM D8071 measurements. The relative response factors (RRFs) used in the analysis are also given in Table 2.

	RRFs	Min Mass %	Max Mass %	Avg. SD (mass %)
Paraffins	0.769	6.88	14.01	0.11
Isoparaffins	0.781	32.55	52.92	0.24
Olefins	0.465	1.95	16.09	0.19
Naphthenes	0.786	2.73	14.66	0.18
Aromatics	0.296	16.11	31.26	0.14
Ethanol	1.029	0.00	10.71	0.05
Iso-octane	0.674	2.67	21.97	0.07
Naphthalene	0.207	0.09	0.30	0.00
Methylnaphthalenes	0.250	0.06	0.52	0.00
Benzene	0.258	0.08	1.06	0.00
Toluene	0.267	1.70	8.13	0.03
Ethylbenzene	0.284	0.27	1.70	0.01
Total Xylenes	0.284	1.50	9.25	0.04

Table 2: Relative Response Factors (RRFs) used by ASTM D8071 for PIONA analysis in finished gasoline, as well as the range and standard deviation of mass % values determined for 13 proficiency samples.

The results obtained with D8071 were compared to data from alternative ASTM methods documented in proficiency reports. Figure 4 displays selected examples of the high-level of agreement between D8071 and other ASTM measurements. The results show good agreement in terms of sample-to-sample process changes in the defined parameters.

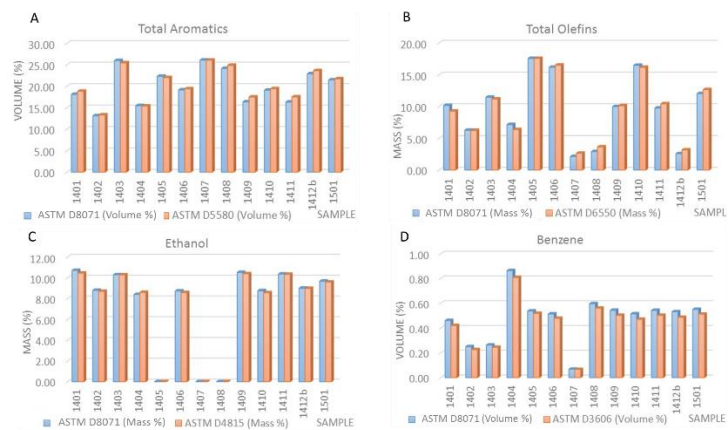


Figure 4: Comparison of results obtained by the ASTM D8071 and alternative ASTM methods; A) total aromatics, B) total olefin, C) ethanol, and D) benzene.

Separate studies have shown comparability of D8071 results with D6729, D5443, D6839, and D1319.<sup>3,5</sup> It is very important to note that these ASTM methods either require complex instrumentation, take two to three hours to perform, or are not comprehensive in their analysis of PIONA parameters. ASTM D8071 can be completed in approximately 30 min, and the TID analysis performed by VUV Analyze™ software can be executed in 1 – 2 minutes. Moreover, the GC-VUV based method can characterize all relevant parameters in a single run. Legacy ASTM methods D6730 and ASTM D6839 are both capable of PIONA class breakdown and varying degrees of speciation. Because these alternative methods use flame ionization detection (FID), precise control of separation conditions and retention times is necessary for classification or speciation. These methods are therefore more prone to error and less amenable to production control environments.

## Conclusion

ASTM D8071 via VUV PIONA+ has been demonstrated to provide reliable PIONA compound class characterization and analyte speciation for finished gasoline samples. VUV PIONA+ enables automated data analysis that includes clear resolution of co-eluting compounds. Results obtained using ASTM D8071 compared favorably to measurements made by alternative ASTM methods for gasoline analysis. The GC-VUV method run time, as well as data processing and review times, are significantly shorter than legacy ASTM methods. Most importantly, all PIONA compound class information acquired using ASTM D8071 was obtained with a single injection. VUV PIONA+ provides comprehensive gasoline compositional analysis that is verified by unambiguous VUV spectral library data.

For more detailed information please visit our website at [www.vuvanalytics.com](http://www.vuvanalytics.com), or contact us at [info@vuvanalytics.com](mailto:info@vuvanalytics.com)

## Acknowledgements

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