

PIONA Analysis by the VUV PIONA+ Method

An Application of ASTM Method D8071 for Finished Gasoline Analysis

Introduction

VUV Analytics, Inc. (Austin, TX) announced in December of 2016 the approval of ASTM Method D8071 for finished gasoline samples by GC-VUV. It was approved 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)" and is based on the use of the VGA-100, the world's first vacuum ultraviolet (VUV) absorption detector for gas chromatography (GC).

GC-VUV data is inherently three dimensional and specific to compound chemical structure, allowing some of the separation to occur at the detector. This means that standard analyses that previously required complex chromatographic separation can be simplified and shortened due to the ability to deconvolve overlapping spectral responses. VUV absorbance spectra are typically highly structured and distinct for individual compounds, yet exhibit the intuitive property of having similar features when measuring related compound classes.

Measurement of bulk composition of hydrocarbon groups and individual compounds in gasoline is important for quality control as well as 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., a fit criteria or similar), and instead rely on precise definition and control of retention times, resulting in more error-prone production measurements.

VUV Analytics' first released application, called VUV PIONA+, uses GC-VUV to improve detailed and bulk classification analysis of petroleum-based fuels. The VUV PIONA+ application is fully compliant with ASTM Method D8071 for gasoline analysis by GC-VUV. The result is the potential for GC-VUV to significantly reduce complexity or run times compared to legacy ASTM methods for fuel analysis, as well as the potential of combining information obtained using multiple methods. The VUV PIONA+ method results in a per-measurement information set that would typically require implementation of multiple ASTM methods (e.g. D5769, D5580, D1319, D6550, D3606, D4815, D5599, D5845) while being inherently more robust and production-worthy than the more comprehensive ASTM gasoline methods.



The VUV PIONA+ method uses relatively simple instrumentation: a gas chromatograph, a standard 30m nonpolar column, and a VGA-100 detector. It utilizes a software engine called VUV Analyze™ that provides automated compositional analysis. Bulk concentrations of the hydrocarbon classes of paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) are determined using VUV Analyze™. Specific analytes can also be singled out for further characterization, for example individual oxygenates or aromatics belonging to the BTEX complex.

The setup procedure is straight-forward, with no pre-column tuning or valve timing adjustments. Additionally, analyses are faster given that the method can handle co-elution among various species and hydrocarbon classes. To provide a more advanced means for deconvolution of complex mixtures, a new 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 VUV PIONA+ capabilities 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 λ is the wavelength, and ϵ 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 primarily eluted between 1.5 and 25 minutes in a 30 meter nonpolar phase capillary GC column method. 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 are 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. This same method utilizing a 60 meter column enables the individual compounds (up to C6) to be chemically speciated in addition to being grouped by class.

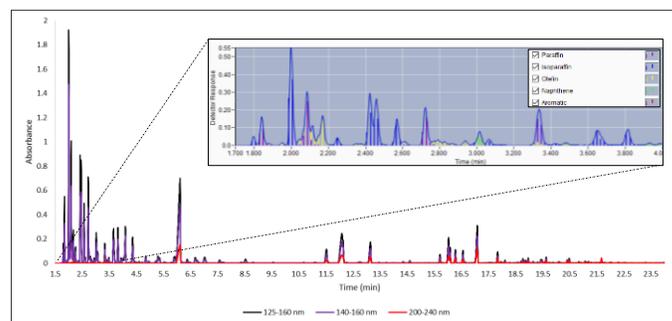


Figure 1: Gas chromatogram of gasoline sample. Inset figure shows zoomed-in retention window with high concentration of PIONA compounds.

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 can be automated to provide class identification

and quantitation of chromatogram peaks within seconds. Figure 2 inset shows the VUV absorbance spectrum and fit of an olefin compound between 2.0 and 2.2 minutes. VUV Verified technology enables the analyte absorbance data to be rapidly compared to the known spectral profiles of PIONA compounds. The analyte 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. This VUV PIONA+ methodology eliminates the compound/class identification error inherent to alternative detection technologies.

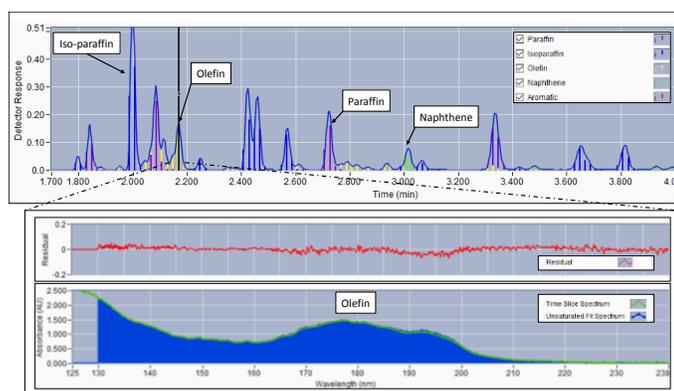


Figure 2: Zoomed-in chromatogram of gasoline sample with key PIONA compound class representative peaks labeled. Inset figure shows olefin spectral and residual fit data.

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 percent of PIONA classes relative to each other. Not shown in the table is a small proportion of oxygenates (~4%) that were identified and 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.

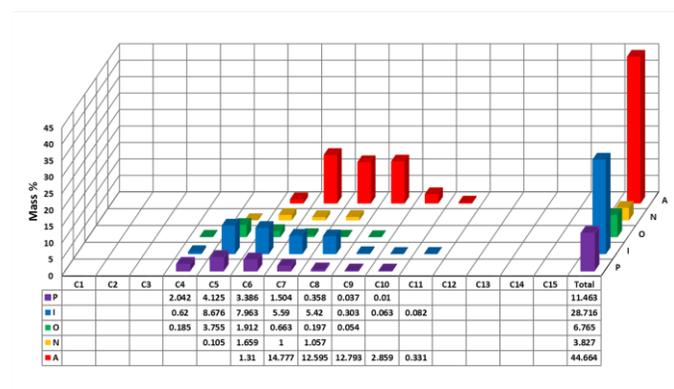


Table 1: Carbon number and mass % composition of the PIONA compounds featured in Fig 1 and 2.

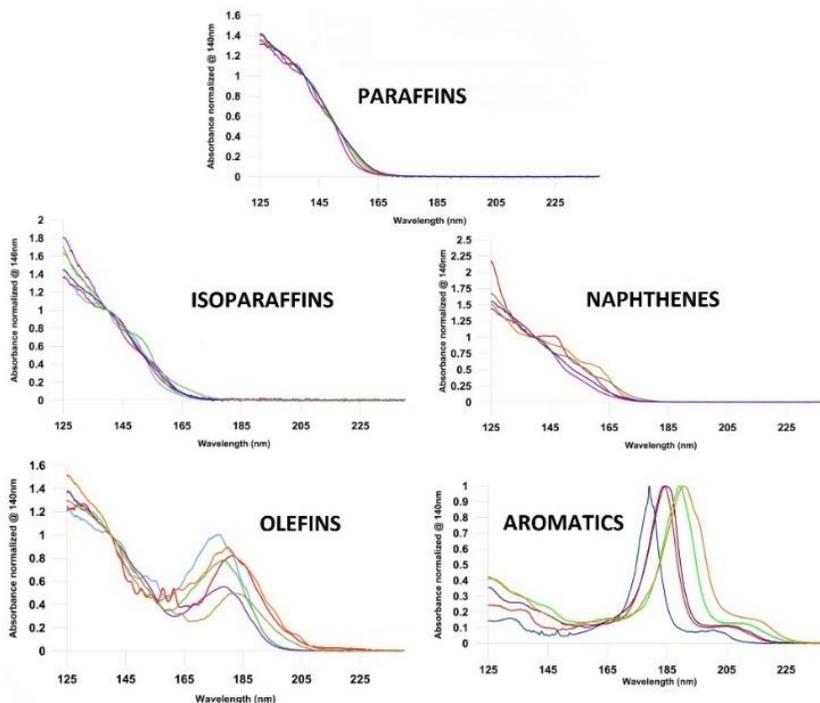


Figure 3: VUV absorbance spectra of PIONA compounds. Each compound class displays distinct spectral features, yet spectra within each category are distinct and lead to individual compound speciation.

Figure 3 demonstrates the detection capabilities inherent to VUV absorbance spectroscopy and exploited by VUV Analyze™ software. 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.

The TID methodology was applied to 13 ASTM proficiency samples (Table 2). The total analysis time is approximately 34 minutes, although all compounds of interest are typically eluted closer to 30 minutes. Each measurement simultaneously determined bulk paraffin, isoparaffin, olefin, naphthene, and aromatics class mass %, along with individual ethanol, iso-octane, benzene, toluene, ethylbenzene, total xylene, naphthalene, and total methylnaphthalene content. Table 2 shows the range of values for these parameters over the entire 13 sample set, illustrating the range of process variation covered by the GC-VUV measurements. The relative response factors 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: RRFs used for PIONA analysis, as well as the range and standard deviation of mass % values determined for the 13 samples.

It is very important to note that legacy ASTM methods either require complex instrumentation, take two to three hours to perform, or are not comprehensive in their analysis of PIONA parameters. The VUV PIONA+ method only requires 30 min per sample run, and the TID analysis can be executed in 30 seconds using the VUV Analyze™ software. Moreover, the GC-VUV can analyze all relevant parameters in one run. Legacy ASTM methods D6730 and ASTM D6839 are both capable of PIONA class breakdown and varying degrees of speciation. However, because these methods use flame ionization detection (FID), precise control of separation conditions and retention times is required for classification or speciation. These methods are therefore more prone to error and less amenable to production control environments.

The results obtained with the GC-VUV were compared to the data reported in the ASTM proficiency reports. Figure 4 shows selected examples of the high level of agreement between the GC-VUV measurements and the ASTM measurements. All of the measurements agree quite well in terms of the sample-to-sample process changes in the defined parameters

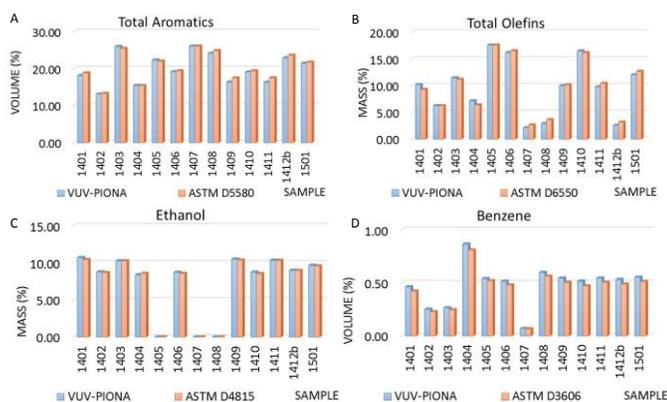


Figure 4: Comparison of results obtained by the GC-VUV and ASTM methods; A) total aromatics, B) total olefin, C) ethanol, and D) benzene.

Conclusion

A new, commercially available PIONA analysis method was applied for the bulk characterization and speciation of finished gasoline samples. Results obtained using the ASTM Method D8071 compliant VUV PIONA+ application compared favorably to those made by other standard ASTM methods. The GC-VUV analysis and data treatment could be performed in less time (34 min runtime) than many legacy alternative approaches. Most importantly, all of the PIONA compound class information was obtained with a single injection. VUV PIONA+ provides a comprehensive gasoline composition method that is verified by unambiguous spectral library data.

For more detailed information please visit our website at www.vuvanalytics.com, or contact us at info@vuvanalytics.com.

Acknowledgements

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2. P. Walsh, M. Garbalena, K.A. Schug, Rapid analysis and time interval deconvolution for comprehensive fuel compound group classification and speciation using gas chromatography – vacuum ultraviolet spectroscopy, *Anal. Chem.*, 2016, 88 (22), pp 11130–11138.
3. ASTM D8071-17, Standard Test Method for 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), ASTM International, West Conshohocken, PA, 2017, www.astm.org



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