NOVEL DETECTOR DRAMATICALLY SIMPLIFIES PIONA ANALYSIS

VUV Analytics, Inc. (Austin, TX) announced in 2015 an analysis engine called **VUV Analyze** which allowed the company to introduce application specific solutions based upon the **VGA-100**, the world's first vacuum ultraviolet (VUV) absorption GC detector. GC-VUV absorbance 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.

The **VUV Analyze** engine implements equations and fit procedures that result in deconvolution of absorbance spectra that contain contributions from multiple species, is capable of binning and storing response contributions from each deconvolution

analysis, and reporting a combined total response at the end of the analysis. 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.

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/
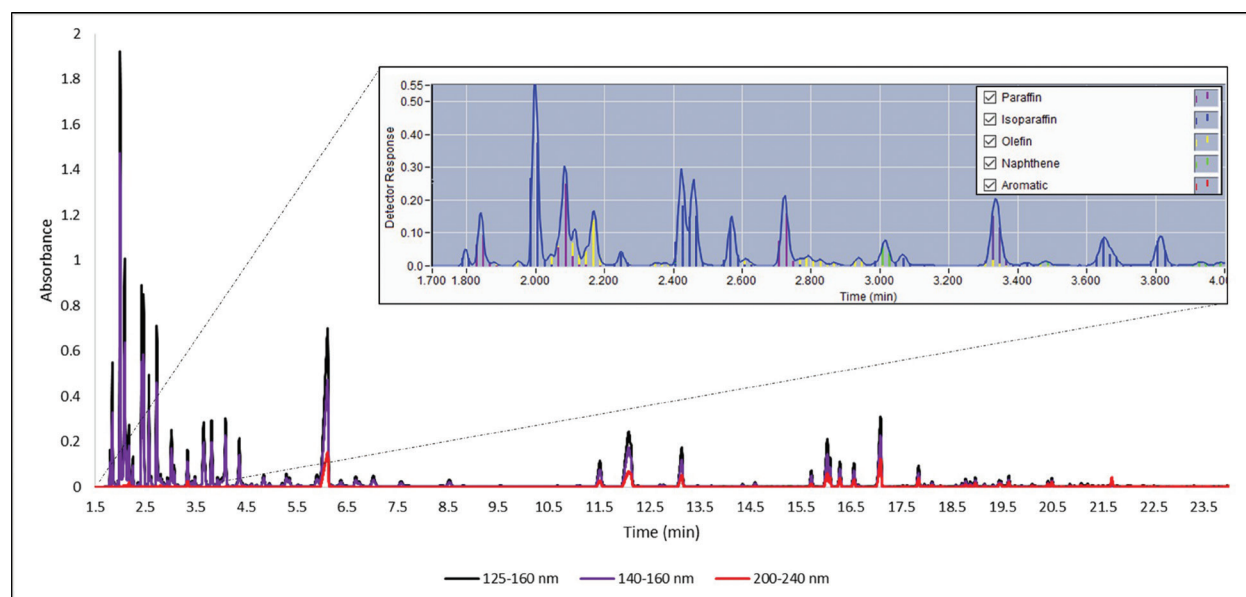

Figure 1: Gas chromatogram of gasoline sample. Inset figure shows zoomed-in retention window with high concentration of PIONA compounds.
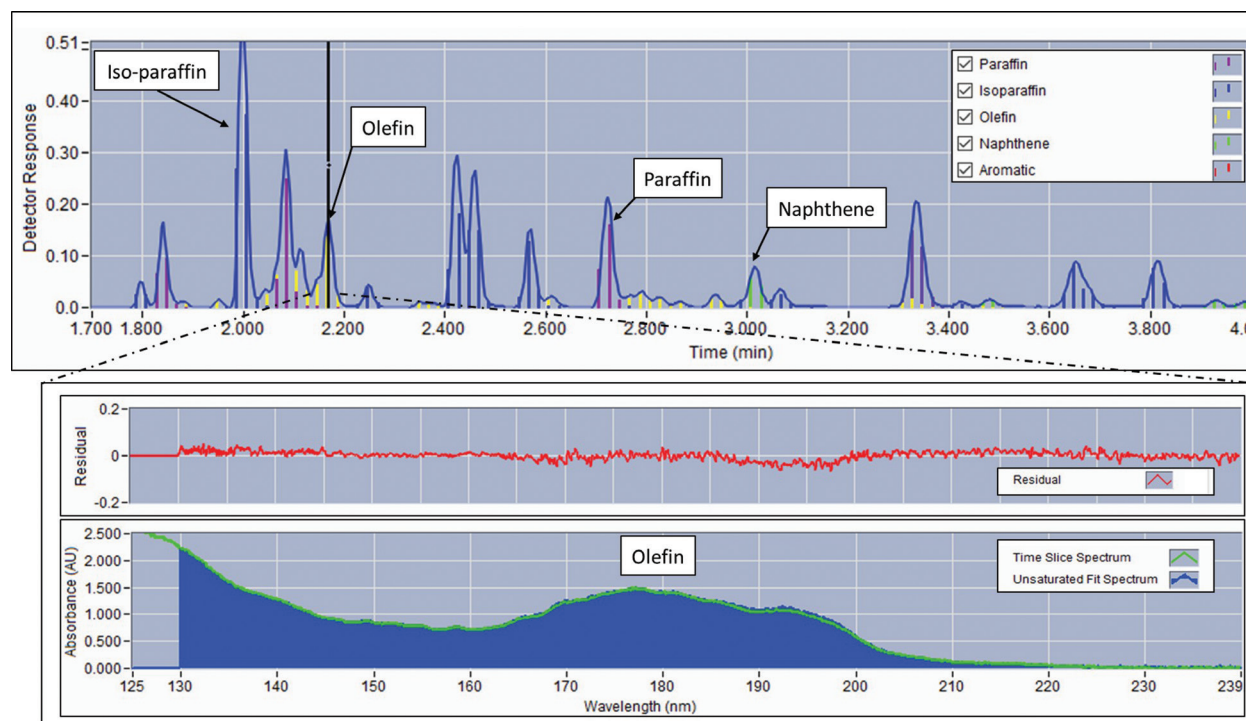

Figure 2: Zoomed-in chromatogram of gasoline sample with key PIONA compound class representative peaks labeled. Inset figure shows olefin spectral and residual fit data.

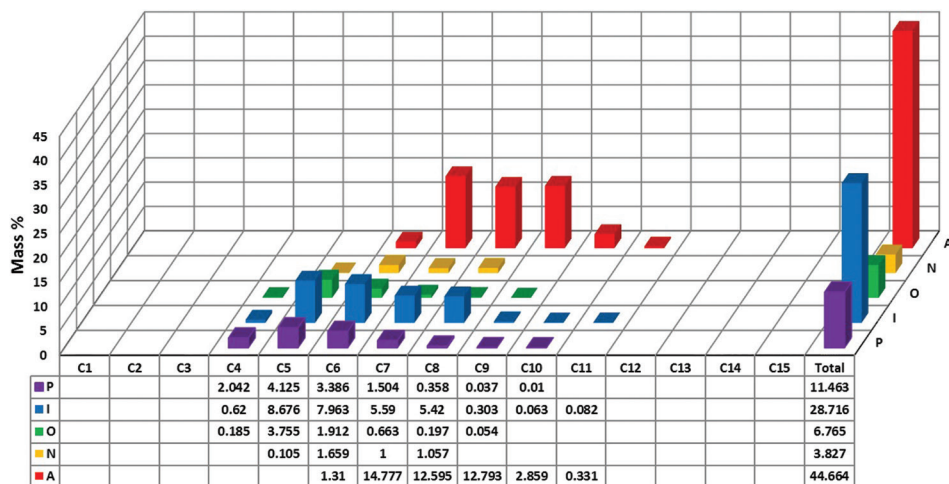|	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	Total
P				2.042	4.125	3.386	1.504	0.358	0.037	0.01						11.463
I					0.62	8.676	7.963	5.59	5.42	0.303	0.063	0.082				28.716
O					0.185	3.755	1.912	0.663	0.197	0.054						6.765
N						0.105	1.659	1	1.057							3.827
A							1.31	14.777	12.595	12.793	2.859	0.331				44.664

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

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 result is the potential for GC-VUV to significantly reduce the complexity or run times compared to existing 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** detector. Bulk concentrations of the hydrocarbon classes of paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) are determined. 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.

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 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 PIONA+** 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.

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 PIONA+ 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
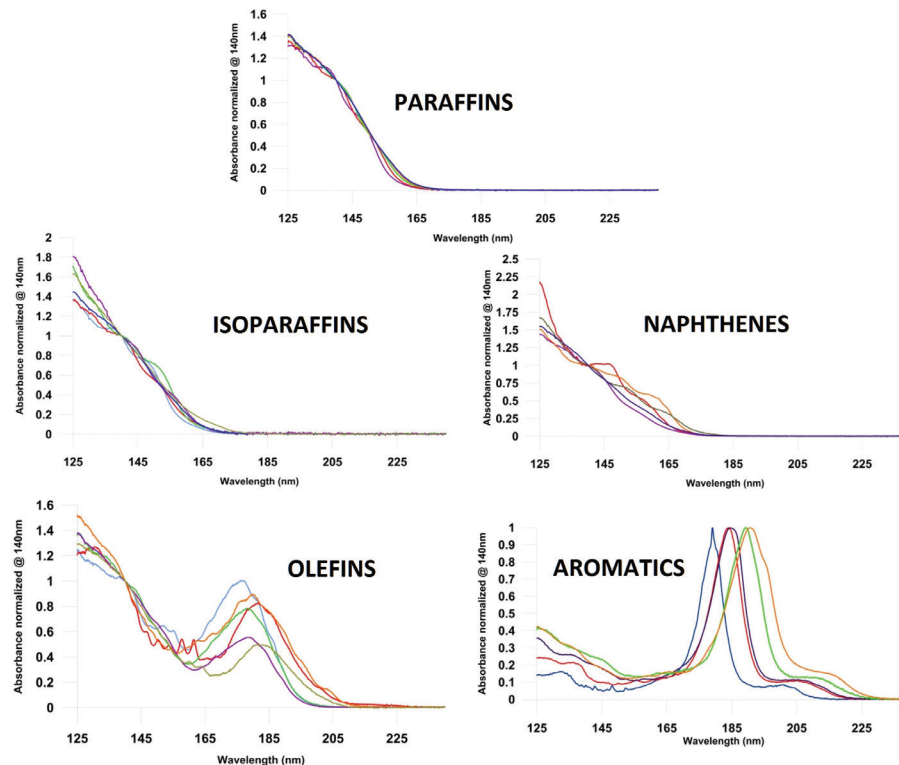

Figure 3: VUV absorbance spectra of PIONA compounds. Each compound class displays distinct spectral features, yet spectra within each category are distinct and lead to individual compound speciation.

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.

Table 1 displays the carbon number and mass % composition of the PIONA compounds featured in Fig 1 and 2. The VUV PIONA+ 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 PIONA+** software.

Figure 3 demonstrates the detection capabilities inherent to VUV absorbance spectroscopy and exploited by **VUV PIONA+** 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. **VUV PIONA+** software contains spectral library data that enables automated PIONA compound characterization.

Author Contact Details

Paul Johnson • **VUV Analytics, Inc.**, 715 Discovery Blvd #502, Cedar Park, TX 78613 • **Web: www.vuvanalytics.com**