VUV PIONA⁺ Analyzer

Technical Summary

The VGA-100 is the world's first benchtop vacuum ultraviolet (VUV) spectrometer for gas chromatography (GC). It is a universal GC detector that provides both qualitative and quantitative data. The strong absorption of gas phase molecules in the VUV region of the ultraviolet spectrum (120 – 240 nm) provide excellent sensitivity, and the compound-specific absorption spectra provide unparalleled selectivity. The VUV PIONA⁺ Analyzer is a VGA-100 pre-configured for the determination of paraffins, isoparaffins, olefins, naphthenes, aromatics, ethanol, and methanol in automotive spark-ignition engine fuels and other gasoline range streams using gas chromatography and vacuum ultraviolet detection (GC-VUV).

A Push-Button Solution that Features:

- Single injection PIONA compound class analysis
- Single 30m Rxi-1ms column
- 34-minute total analysis time
- No traps, pre-column tuning, or calibration requirements
- No special setup
- ASTM method D8071 Compliance
- Customizable individual compound speciation including BTEX aromatics

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System Description

The VUV PIONA$^+$ Analyzer is a VGA-100 Gas Chromatography (GC) detector configured for PIONA compound analysis by the VUV PIONA$^+$ method. The VUV PIONA$^+$ method uses relatively simple instrumentation: a gas chromatograph, a standard 30m nonpolar column, and a VGA-100 detector. It is suitable for use with finished gasoline, reformate, reformer feed, FCC, light naphtha, and heavy naphtha samples. VUV PIONA$^+$ utilizes a software engine called VUV Analyze^{TM} that provides automated compositional analysis. Bulk concentrations of the hydrocarbon classes of paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) are determined using the VUV Analyze^{TM} software package included with the VUV PIONA$^+$ Analyzer. Specific analytes can also be singled out for further characterization, such as individual oxygenates or aromatics belonging to the BTEX complex. VUV PIONA$^+$ is fully compliant with ASTM Method D8071 for finished gasoline samples by GC-VUV.

The VUV PIONA$^+$ Analyzer includes a VGA-100 GC detector, VUV Analyze^{TM} automated compositional software configured for PIONA analysis, and a gasoline component VUV spectral library. The VUV Analyze^{TM} software package features pre-configuration of the VUV gasoline library, PIONA compound response factors, and PIONA compound retention indices. The result is automated PIONA compositional analysis that provides carbon number and mass % while taking <1 min to perform post-run processing.

The VUV PIONA$^+$ method setup procedure is straight-forward, with no pre-column tuning or valve timing adjustments. Additionally, analyses are faster than legacy methods given that VUV Analyze^{TM} can handle co-elution among various species and hydrocarbon classes. PIONA compounds can be speciated through C6, and PIONA compound classes are characterized >C6. Typical method conditions are detailed below, but column and gas chromatograph vendors may vary. VUV detectors work with any gas chromatograph and do not require use of an applicated GC.

DETECTOR	VUV ANALYTICS VGA-100 GC DETECTOR
Gas Chromatograph	Agilent 6890 equipped with a 7683 model autosampler
Column	Restek 30m x 0.25mm x 0.25µm Rxi-1ms
Column Type, Column Phase	Capillary, Nonpolar
Injector Temperature	250 °C
Injection Volume	0.3 µL
Split Ratio	50:1
Column Flow	1 mL/min
Oven Initial Temperature	35 °C
Initial Hold Time	10 min

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Oven Ramp	7 °C/min
Final Oven Temperature	200 °C
Final Hold Time	0 min
Detector Makeup Gas Pressure (gauge)	0.25 psi
Detector Scan Time	11 ms
Detector Averages per Scan	20
Detector Flow and Transfer Tube Cell Temperature	275 °C

The ASTM D8071 and VUV-PIONA+ methods provide equivalent PIONA compound information that would otherwise require the use of multiple ASTM methods with complex setups and instrumentation. The table below shows how ASTM Method D8071 can be substituted for these methods.

VUV-PIONA+	ASTM METHOD(S)	
Mass % of		
P		ASTM D6839 ASTM D6730 **ASTM D8071**
I		
O	ASTM D1319 ASTM D6550	
N		
A	ASTM D1319, ASTM D5580, ASTM D5769	
Total Saturates	ASTM D1319	
Ethanol	ASTM D4815, ASTM D5599, ASTM D5845	
Benzene	ASTM D3606, ASTM D5580, ASTM D5769	
Toluene	ASTM D3606, ASTM D5580, ASTM D5769	
Ethylbenzene	ASTM D5580	ASTM D6730 **ASTM D8071**
m,p,o-Xylene	ASTM D5580	

V U V   A N A L Y T I C S

Instrument Specifications

PARAMETER	VUV ANALYTICS VGA 100	NOTES
Light Source	Deuterium lamp	
Wavelength Range	120 - 240 nm	
Wavelength Accuracy	±0.2 nm	
Wavelength Reproducibility	0.05 nm	
Type of Response	Universal	*H_2, He, Ar are transparent
Spectral Bandwidth	<1 nm	
Maximum Acquisition Rate	>90 Hz	
Data Collection Interval	11 ms	
Response Characteristic	Absorption versus Wavelength	
Measurement Output	Identity, Concentration	
Detected Species	All compounds and classes	*H_2, He, Ar are transparent
Typical IDLs (pg on Column)	n-Decane (C10): 40 n-Eicosane (C20): 32 n-Triacontane (C30): 35 n-Tetracontane(C40): 55	
Linear Range	3-4 orders	
Temperature Range	Ambient - 300° C	
Carrier Gases	H_2, N_2, or He	
Makeup gas	Ar, He, N_2	
Flow Cell Dimensions	10 cm path length, <80 µL cell volume	
Instrument Dimensions	30" x 13" x 17", or 76.2 x 33 x 43.2 cm	
Deuterium Lamp Lifetime (hours)	>2000	Lamp intensity half- life at 250 nm
Weight	120lbs, or 54.4kg	
Power Input Voltage	100/240V	
Power Consumption	<700 VA	
Operating System Requirements	Quad Core processor, 1080 x 1920 Monitor, Minimum Memory 8G, Hard Drive Min 250G, Windows 7, 8, or 10 (64 bit)	
Additional Facilities Requirements	CDA connection 99.999% N_2 connection, typical 40 mL/min purge requirement	

System Configuration

The VUV PIONA+ Analyzer includes a VGA-100 Gas Chromatography detector, VUV Analyze™ automated compositional software configured for PIONA compound analysis, and a gasoline component VUV spectral library. The table below provides details of each component.

PART NUMBER	VUV PIONA+ ANALYZER: VACUUM ULTRAVIOLET GAS CHROMOTAGRAPHY DETECTOR FOR PIONA COMPOUND ANALYSIS
E11-0010-010	VGA-100 Vacuum Ultraviolet Gas Chromatography Detector
	Standard Features include:
	1. Fully Automated Measurement
	a. Broad Spectral Range Absorption Measurements
	i. 120 to 240nm
	b. >90 Hz acquisition rate
	2. Easy integration onto most GC platforms
	a. Integrated transfer tube programmable up to 300°C
	i. Fits into most GC / MS ports
	b. Sample cell with inert coating programmable up to 300°C
	i. <80uL volume
	c. GC synchronization start/stop trigger
	VUVision Software Package (included with E11-0010-010)
	Windows 7 or 8.1 Based Application Software
	1. VUVision Control and Data Analysis
	Chromatographic and Spectral Data Review GUI
	2. VUV Library - Base Compound Set
	User editable VUV absorption cross-section library
S11-0011-VGA	**VUV Analyze™ - Automated VUV Spectral Fitting**
	a. Automated compound identification and quantification
	b. Tiered library search and automated co-elution analysis
	c. Time segmented analysis for complex chromatograms
S11-0012-PIONA	**PIONA Analysis Configuration Upgrade**
	Includes configuration of VUV library, response factors, retention indices, and method conditions for PIONA analysis
S11-0021-VGA	**Gasoline Component Set Library**
	a. User editable VUV absorption cross-section library
	b. Includes complete Gasoline Range compound library
	c. Compound Speciation through C6, class representation >C6

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System Software

The VGA-100 is powered by VUVision software, which is included with the detector. VUVision is the base software for system control, data acquisition, library searching, qualitative analysis, calibration, and quantitative analysis by external or internal standard methods. The VUV PIONA$^+$ Analyzer package additionally includes VUV Analyze™ automated compositional software configured for PIONA compound analysis along with a gasoline component set library.

VUVision Software

VUVision software simplifies GC analysis by providing an intuitive interface for analyte characterization by VUV spectroscopy. VUVision delivers straightforward workflows for acquiring and processing data, resulting in high automation confidence and low-risk of analytical error. This robust software solution delivers standard chromatographic capabilities and data analysis while providing spectral information that is unique to VUV spectroscopy. A typical home screen workflow is shown below.
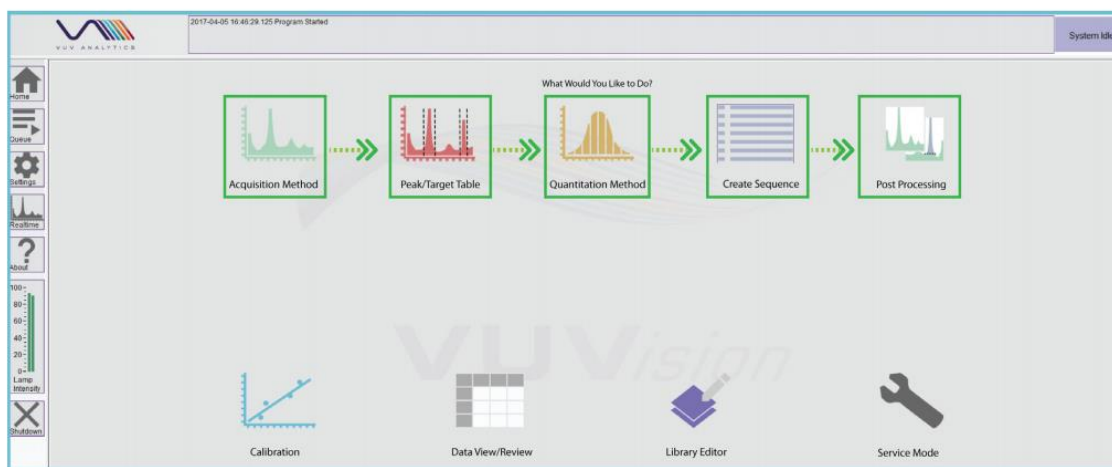

VUV Analyze™

VUV Analyze™ is an automated post-run compositional analysis software option included with the VUV PIONA$^+$ Analyzer. Its VUV library, response factors, and retention indices are configured for PIONA compound analysis. It performs rapid post-run analysis of compound classes and carbon number that typically takes <1 min per sample to complete. An example of VUV Analyze™ PIONA compound characterization is shown below.
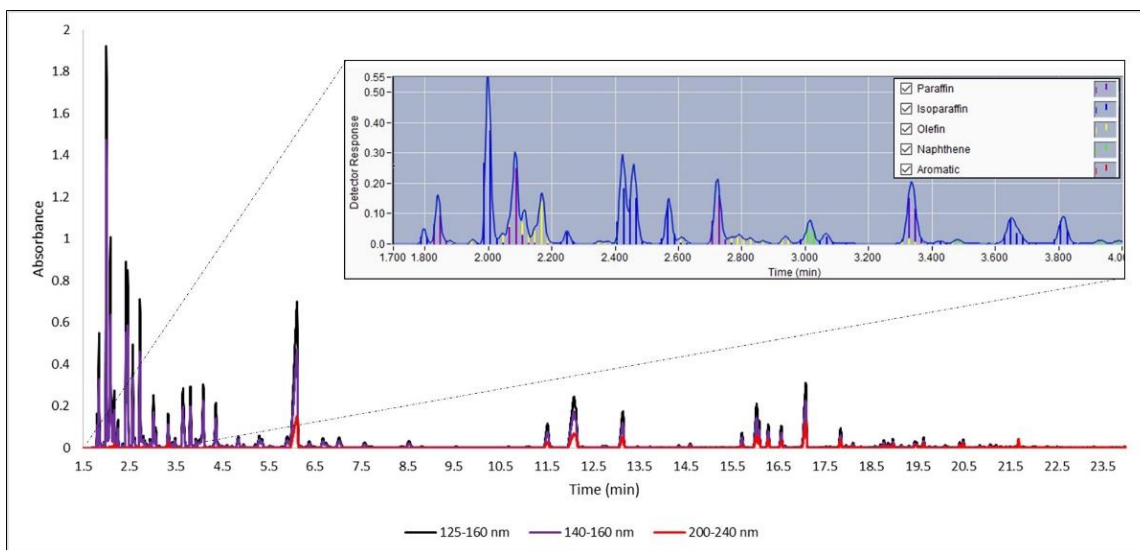
VUV Analyze™ Provides Automated PIONA Analysis of Complex Gasoline Samples:
Gas chromatogram of representative ASTM proficiency gasoline sample. Inset figure shows zoomed-in retention window with high concentration of PIONA compounds.
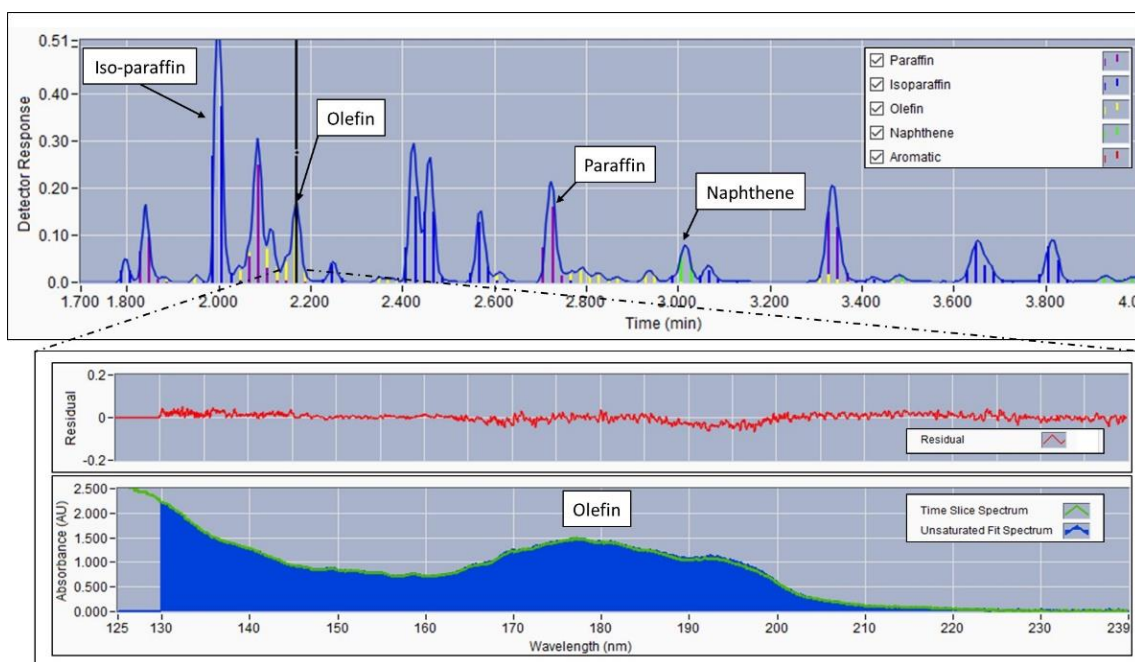
Every Time Slice Contains Both Chromatographic and Spectral Data, and Fitting is Automated by Analyze™:
Zoomed-in chromatogram of representative ASTM proficiency gasoline sample with key PIONA compound class representative peaks labeled. Inset figure shows olefin spectral and residual fit data. Key chromatographic peaks representing Paraffin, Isoparaffin, Olefin, and Naphthene compounds in the 1.5 – 4.5 minute retention time window are labelled. VUV Analyze™ software can rapidly identify these compound classes based on their distinct spectral characteristics.
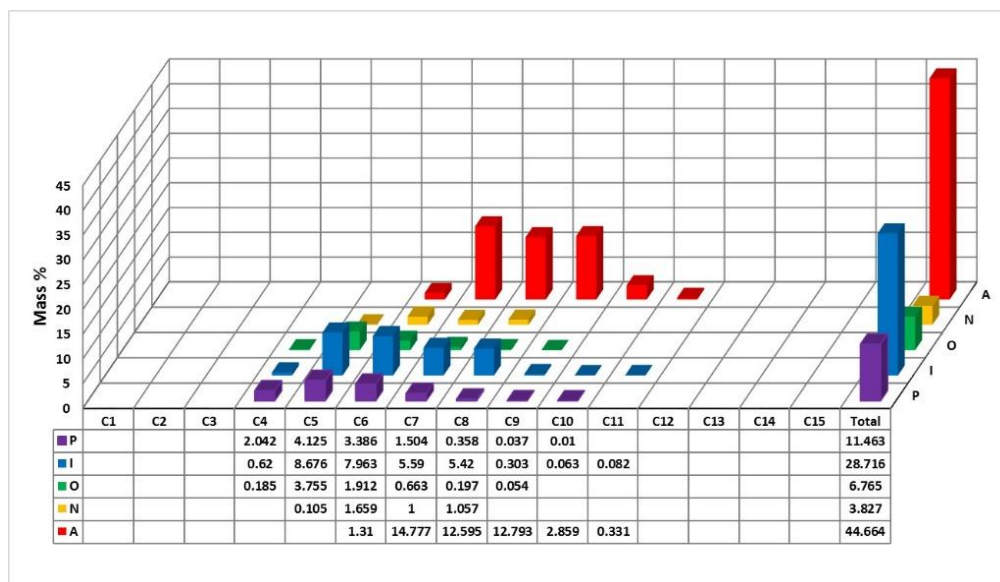
Compositional Analysis Results in Compound Class and Carbon Number Reporting: Carbon number and mass % composition of PIONA compounds in representative ASTM proficiency gasoline sample.

	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

Performance Data

The VUV PIONA[+] method was applied to 13 ASTM proficiency samples. The total analysis time was 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. The table below 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 (RRFs) used in the analysis are also provided.

COMPOUND CLASS	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

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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

Optional Accessories

The only consumable item requiring occasional replacement is the VGA-100 deuterium lamp. It's rated >2000 hours and its ordering information is shown below. Replacement transfer lines and flow cells, flow cell refurbishment, and service and preventative maintenance plans may also be ordered by contacting VUV Sales. Gas chromatographs, columns, and standards are sold separately.

NUMBER	VUV PIONA+ ANALYZER: Consumables & Options
E12-0330-010	**Deuterium Lamp Assembly**
	a. Includes lamp and quick-change housing assembly
	b. Rated for >2000 hours (lamp intensity half-life at 250 nm)
E12-0010-020	**Replacement Flow Cell**
	Replacement Flow Cell (High Volume; <80uL volume) - includes full flow cell assembly and thermal isolation adapters
E12-0010-020-R	**Flow Cell Refurbishment** Includes new windows, O-rings, seals, ultrasonic clean, and inert coating
M13-0011-SC	**1 Year Service Contract**
	Includes extended HW & SW warranty + preventative maintenance for 1 year
M13-0013-PM	**Preventative Maintenance - 3 Year Plan**
	3-year annual preventative maintenance plan
VUV1*	**System Validation Mixture**
	Custom VUV Analytics PIANO Standard - 1X1 mL Ampoule

*sold by Spectrum Quality Standards with part number VUV1, contact sales@spectrumstandards.com

Installation & System Requirements

Installation Space Considerations

The instrument requires a clear surface minimum of 74cm (29in) deep by 41cm (16in) wide by 42cm (16.5in) high, and capable of supporting at least 54kg (120lbs). If additional support equipment is placed on the same benchtop as the instrument, then

the surface must be capable of supporting at least the sum of the instrument plus the weights of all additional support equipment. An additional 12cm (5in) must be allowed behind the instrument to allow for plumbing and for the exhaust air to escape the instrument. VGA-100 Gas Chromatography detector external dimensions are shown below.
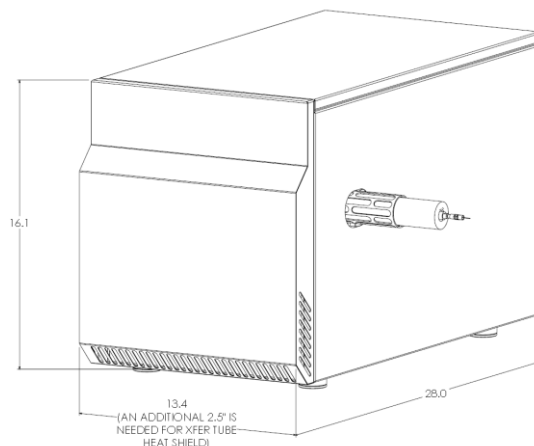
Gas Purity

In general, oxygen, moisture, hydrocarbons (oils), carbon monoxide, carbon dioxide, and halogens in gases supplied to the instrument can cause baseline disturbances and/or damage the detector. "Instrument" or "chromatographic" purity grades of gas specifically intended for chromatographic use are recommended for optimal performance. All gas supplies used to the detector should be in the 99.995% to 99.9995% purity range. In addition, the use of high-quality traps immediately after the main tank pressure regulator are required for optimal performance.

GAS PURITY RECOMMENDATIONS	
Detector Purge and Make-up Gases	
Argon, Helium, and Nitrogen	99.9995%
Detector Support Gases	
Air (Clean Dry Air)	Zero-grade or better

Environmental Conditions

The instrument must be installed and operated in the ambient conditions listed below. Furthermore, operating the instrument within the recommended ranges ensures optimum instrument performance and lifetime.

ENVIRONMENTAL CONDITIONS	
Installation Location	Weather Protected (Indoors)
Protection Category	IP20
Temperature	$^+$5C to $^+$40C [1]
Relative Humidity	5 – 80% [2]
Atmospheric Pressure	75kPa – 106kPa
Degree of Pollution	2
Overvoltage Category	II
Altitude	2000

1 – Recommended Temperature Range 20 to 27C
2 – Recommended Humidity Range 50 – 60%
* After exposing the instrument to extreme environments, allow a minimum of 60 minutes for it to return to the recommended ranges prior to data collection.

About VUV Analytics

VUV Analytics' vision is to enable new science and better processes by harnessing the unique capabilities of VUV technology. VUV Analytics is the world leader in vacuum ultraviolet (VUV) absorption spectroscopy. VUV light creates unique spectral signatures that result in the unambiguous identification and quantitation of compounds across a diverse set of markets and applications. Unlike legacy detection methods, VUV detectors allow for a more automated analysis with reduced human error and higher analytical throughput.

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Science in a New Light