VUV ANALYTICS

GLOBAL™ ANALYSER SOLUTIONS G·A·S

PIONA analysis by VUV

- ASTM 8071
- Single column analyser
- Very low operational costs
- Excellent compliance with complex multidimensional method
- Less prone to error than the usual methods

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GAS offers custom configured GC analysers for many application fields since 40 years. GAS analysers are designed to meet many standardised methods from GPA, ASTM, UOP, ISO, EN and others. The efficient configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.

ASTM Method D8071 provides complete PIONA compound class characterisation in a single measurement. GC with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV) from VUV Analytics offers relative simple instrumentation and automated analysis software with short runtimes and more robust and reliable results compared to ASTM D6839, thus having the potential to replace this complex method

Simplified PIONA

PIONA analysis 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, see figure 1. GC-VUV absorbance data is inherently three dimensional (time, absorbance, wavelength) and specific to the compound chemical structure.

VUV Analyze™ software uses equations and fit procedures that result in deconvolution of absorbance spectra with contributions of many species. The software includes a database library of VUV reference spectra, compound class information and physical properties for each hydrocarbon class. Results are reported as mass or volume percent.

Due to the distinct spectra, the method is not dependent on very precise retention times like DHA, which often leads to error-prone results. VUV offers accurate compound speciation up to C_6 and bulk compound class characterisation for the higher carbon numbers.

GC-VUV is covered by ASTM D8071

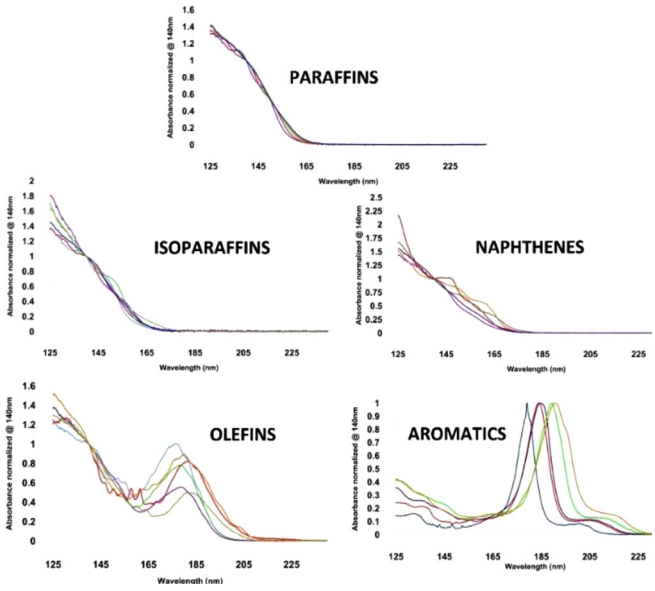
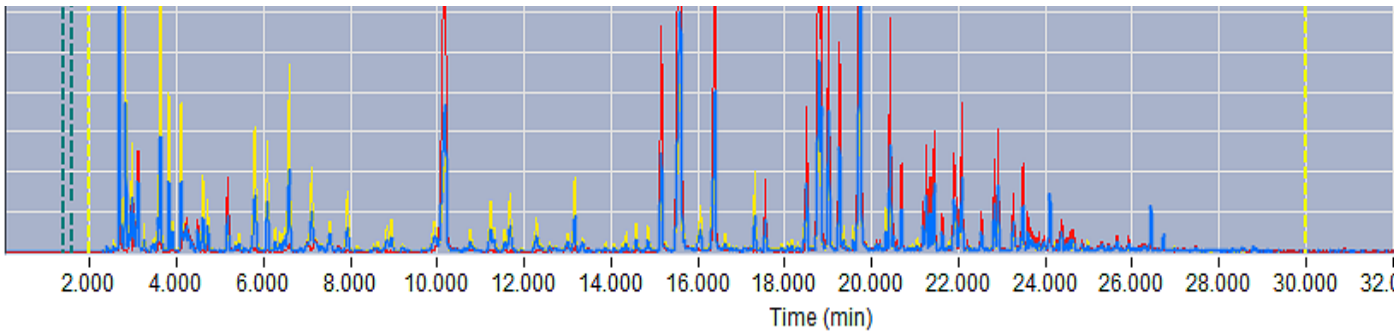


Figure 1. Distinct spectra for PIONA component classes. VUV spectra are highly stable and independent of instrument settings. Reliable identification is also offered for paraffins and iso-paraffins, which apparently have small spectral differences

Figure 2. Example chromatogram by VUV-Analyze™ engine, showing spectral filters 170-200 nm (red, aromatics) and 125-160 nm (yellow, saturates). (The blue graph represents the total signal). The runtime is 34 minutes.



Results

Figures 3 and 4 show a gasoline sample chromatogram with PIONA compounds. Spectral filters can be used as a visualisation tool to assist in discriminating between different compound classes. In this example, 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 figures show 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 and colour coded them appropriately.

Figure 5 displays the carbon number and mass % composition of the PIONA compounds featured in Fig. 3 and 4. 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.

GC-VUV results were compared to data reported in ASTM proficiency reports. Figure 6 shows selected examples of the high level of agreement between GC-VUV and the ASTM measurements. All of the measurements agree very well in terms of the sample-to-sample process changes in the defined parameters

Straight-forward method

VUV-PIONA+ uses straight-forward instrumentation: Thermo Trace GC 1300 gas chromatograph, 30m non-polar column and VGA detector, with easy method setup and low operational costs as a result. Helium or hydrogen is used as carrier gas, and the GC oven does not require cryogenic operation. See figure 7. The total runtime is 34 minutes.

Oxygenates

Specific analytes like oxygenates are analysed as well. VUV analyze™ ensures accurate unambiguous identification of these type of components by fitting absorbance data with the spectral library after deconvolution. No prior knowledge of alcohol or ether content is necessary.

High Olefin Content

ASTM D6839 cannot handle samples that contain a very high Olefin amount, because of overload of the Olefin trap. GC-VUV is based on a single column analysis without traps and column switching, and provides therefore accurate analysis of samples with high olefin content.

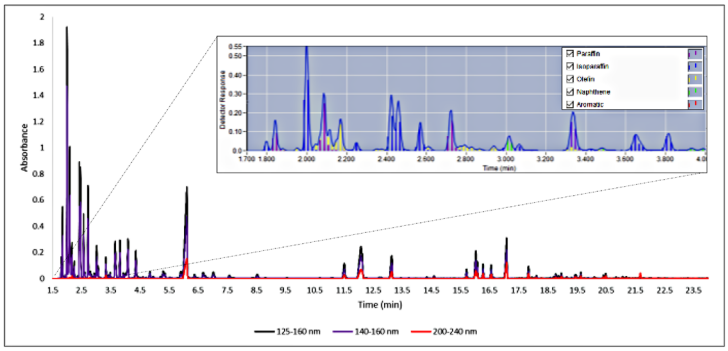


Figure 3. Gas chromatogram of gasoline sample. Inset figure shows zoomed-in retention window with high concentration of PIONA compounds.

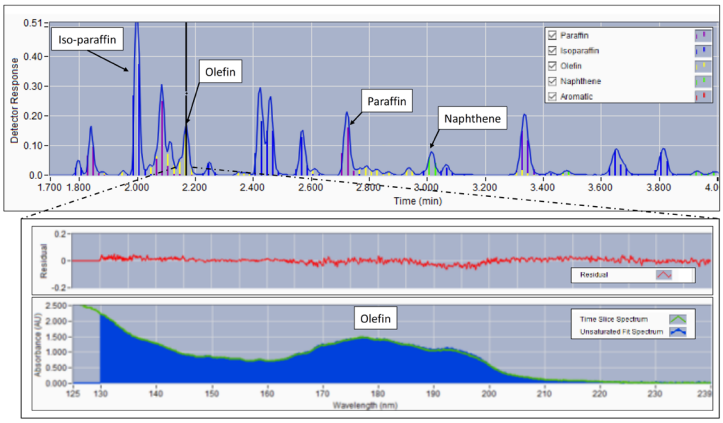


Figure 4. Zoomed-in chromatogram of gasoline sample with key PIONA compound class representative peaks labelled. Inset figure shows olefin spectral and residual fit data.

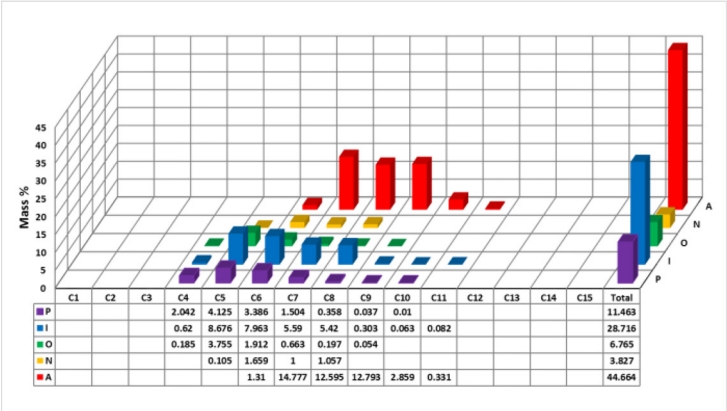


Figure 5. Carbon number and mass % composition of the PIONA compounds featured in Fig 3 and 4.

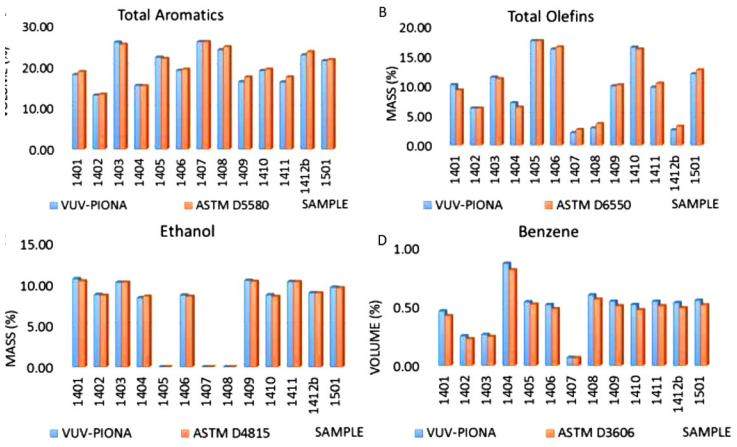


Figure 6. Comparison of results obtained by the GC-VUV and ASTM methods; A) total aromatics, B) total olefin, C) ethanol, and D) benzene.

Specifications:

Standardised method:	ASTM D8071
Application:	Characterisation of PIONA+ (Paraffins, Iso-paraffins, Olefins, Naphthenes, Aromatics, Oxygenates) compounds in various hydrocarbon mixtures.
Configuration:	1 channel instrument with liquid injection and vacuum ultraviolet spectrometer
GC instrument:	Trace GC1300 (Thermo)
Detector:	VGA-100 (VUV Analytics)
Analysis Time:	34 minutes
Column type:	Restek Rtx-1, 30m*0.25mm, df=0.25u
GC oven temperature program:	35 °C (2 min) - 15 °C/min - 200 °C. No cryogenic requirements.
Detector temperature:	275 °C (flow cell); 275 °C (interface)
Minimum detectability:	< 0.05 vol %, depending on component
Linearity:	> 3.5 decades, depending on component
Accuracy:	Better than 1 % RSD
Repeatability:	Better than 1 % RSD
Sample requirements:	See our pre-installation guide for additional requirements

Figure 7. VUV Analytics VGA-100 + Thermo Trace GC1300

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