BEYOND MEASURE

SCION INSTRUMENTS

Determination of Hydrocarbon Group Types in Spark Ignition Fuels using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV)

Application Note AN0021

INTRODUCTION

The VUV detector is the next generation GC detector for PIONA analysis; simplifying the complex analysis of hydrocarbon samples with short analysis times, including spark ignition fuels. There are many challenges within the petrochemical industry and associated GC analysis methods. As regulations continuously drive down the accepted levels of impurities in gasolines, lower detection and quantification levels must be observed when using GC as a method for analysis. Fuel impurities must be removed whilst also retaining and characterising paraffins, iso-paraffins, olefins, napthenes and aromatics (PIONA) as well as other hydrocarbon classes to maintain the octane value of the system.

ASTM D6730 is the standard test method for the determination of individual components in spark ignition fuels using GC-FID. However, this detailed hydrocarbon analysis (DHA) is time consuming with long analyses, column tuning and extensive post processing times. DHA is reliant on reproducible retention index values; requiring optimal controlled operating, flow and temperature conditions, for identification and quantification. Additionally, full gasoline analysis can be completed using multi-dimensional gas chromatography; a highly complex column switching technique to determine carbon number distribution for the different component classes. Due to the sophisticated setup of the multi-dimensional GC; which contains numerous valves, columns and traps, this analysis is expensive and challenging to use.

VUV Analytics have developed a benchtop vacuum ultraviolet (VUV) spectrometer that utilises an ultraviolet spectrum (stored library), retention indices and relative response factors to provide excellent sensitivity and unparalleled selectivity for the analysis of spark ignition fuels, when coupled to a GC. The VUV PIONA+ analyser is preconfigured for the determination of bulk PIONA, specific oxygenates and BTEX (benzene, toluene, ethyl benzene and xylenes) compound content, in a single measurement. In addition, ASTM D8071 is the standard method for the determination of hydrocarbon group types using GC-VUV.

This application note details the analysis of a reference standards along with gasoline, alkylate, reformate and racing fuel samples on the SCION 436 GC with VUV detector according to the ASTM D8071 method.

EXPERIMENTAL

The SCION 436 GC equipped with a 8400 autosampler, S/SL injector and VUV detector was used for the analysis of alkylate, gasoline and a racing fuel sample. Reference standards included a PIONA+ mix and a ASTM P-00800 reference and performance check. Repeatability of the system was completed using a Supelco reformate sample. System suitability was also tested using a benzene standard, in order to calculate the benzene response.

Table 1 details the analytical parameters with Figure 1 showing the analytical instrumentation, used throughout this application.

Table 1. Analytical conditions of the GC-VUV

Conditions	
S/SL	250°C, 0.3µL, split 20:1
Column	30m x 0.25mm x 0.25µm
Oven Programme	35°C (hold 10 min), 7°C/min to 200°C
Carrier Gas	Helium 1mL/min constant
Detector Flow Tube	275°C
Transfer Tube	275°C
Wavelength	125-240nm

Fig 1. SCION 436 GC with VUV detector

RESULTS

The retention indices (RI) and relative response factors (RRF) of all hydrocarbon classes and individual compounds are used during data processing. RRF of the classes and compounds are prep-programmed in the VUV Analyze software.

The VUV detector scans during the GC analysis at a frequency of over 90Hz. The PIONA+ analyser eliminates the issue of complex chromatographic separation as the VUV Analyze software automatically deconvolves overlapping spectral responses. The VUV absorbance spectra is specific to the compound chemical structure. The VUV software is not dependent on very precise retention time. The built in UV spectral library was used to confirm correct peak identification. Additionally, spectral filters can be used as a visualisation tool to assist in discriminating between different compound classes. The spectral filters are applied post data acquisition to enhance analyte sensitivity.

Baseline resolution is not vital using the PIONA+ as the specific UV spectra still accurately identifies and quantifies compounds.

Figures 2-6 show the chromatograms of the ASTM P-00800 reference standard, PIONA reference standard, gasoline sample, alkylate sample and racing fuel sample, respectively.

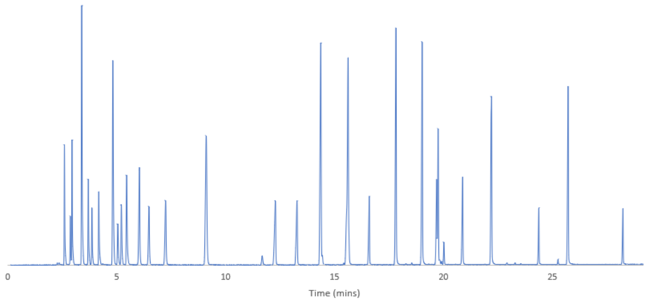

Fig 2. Separation of ASTM D8071 calibration standard

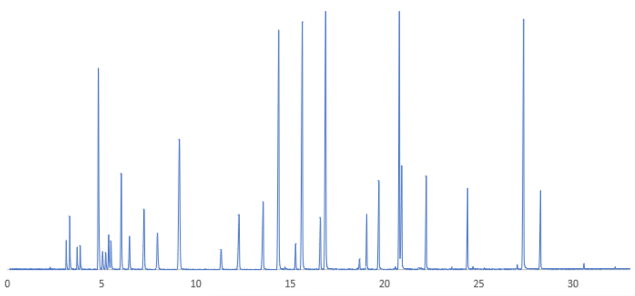

Fig 3. Separation of PIONA calibration standard

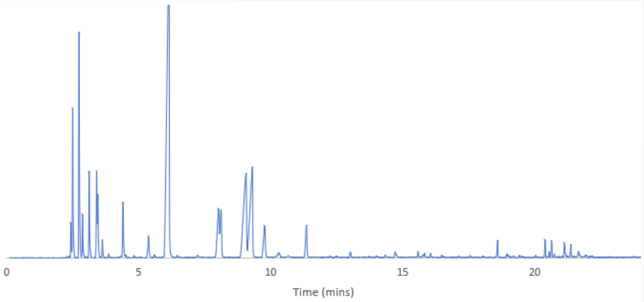

Fig 4. Separation of Alkylate sample

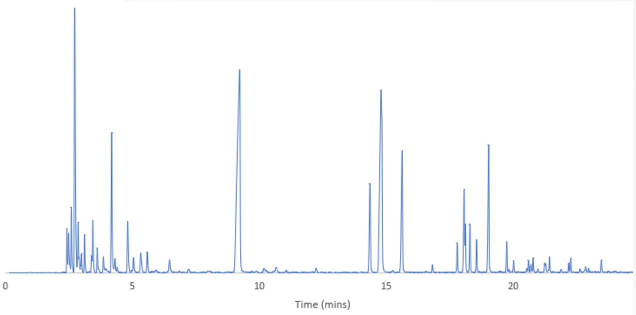

Fig 5. Separation of Gasoline sample

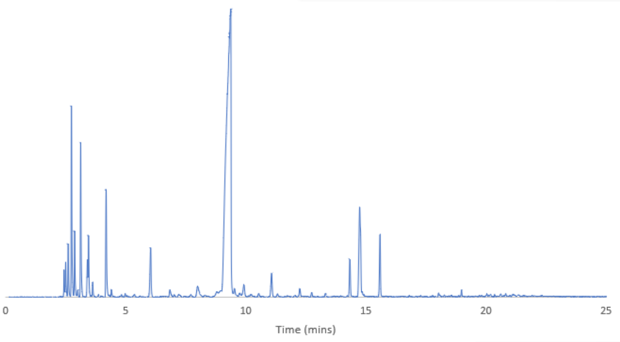

Fig 6. Separation of Racing Fuel sample

Data processing is an automated process through the VUV Analyze software. The PIONA+ analyser divides the total chromatogram time region into individual time slices. Each time slice is then used to calculate the total absorbance. Both mass% and volume% are calculated from the total response contribution of Figures 7-9 detail the comparison of the expected values and actual values of the ASTM P-00800 calibration standard and the PIONA standard results when analysed via the GC-VUV.

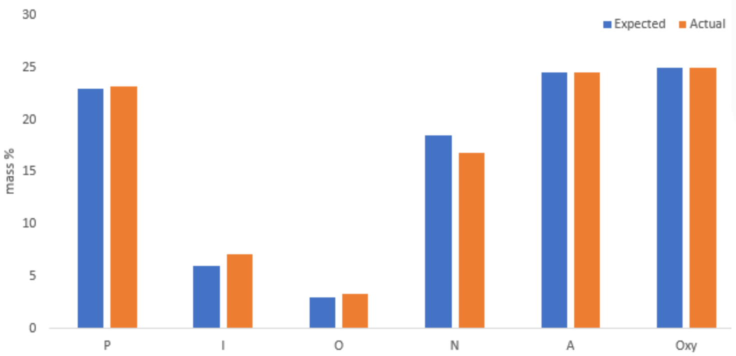

Fig 7. Expected and actual values of hydrocarbon groups ASTM standard (mass%)

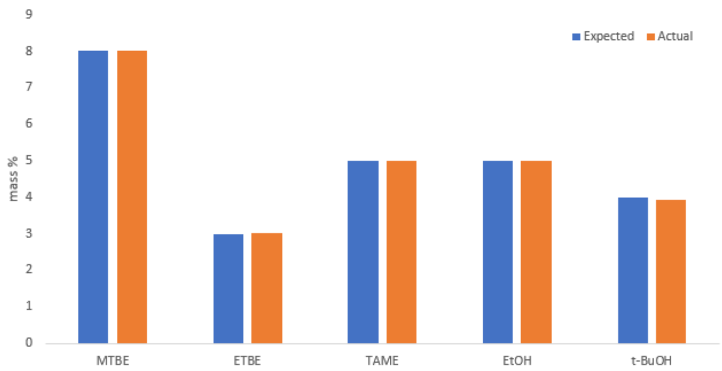

Fig 8. Expected and actual values of individual components ASTM standard (mass%)

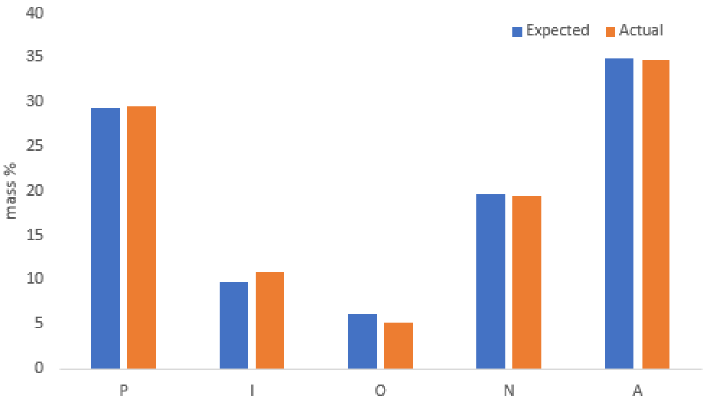

Fig 9. Expected and actual values of hydrocarbon groups PIONA standard (mass%)

The actual and expected results gave comparable results, for both ASTM P-00800 and PIONA standards, highlighting the accuracy of the VUV system.

Table 2 details a typical PIONA report generated by the VUV Analyze software. The hydrocarbon class values, as well as a selection of individual compounds obtained when a gasoline sample was analysed via GC-VUV, is shown.

Table 2. Composition of a gasoline sample (mass%)

	P	I	O	N	A
C4	1.70	1.92	0.32		
C5	2.86	22.31	1.21	0.45	
C6	1.14	6.05	0.61	1.92	0.92
C7	1.00	3.85	0.78	0.54	11.54
C8	0.26	1.81	0.11	0.73	13.00
C9	0.08	0.47		0.05	7.85
C10	0.02	0.11	0.03	0.07	2.17
C11	0.01		0.01		0.15
C12					0.09
C13					
C14					
Total	**7.07**	**36.52**	**3.07**	**3.76**	**35.72**

ETBE	9.15
Ethanol	4.16
Xylenes	9.73

The Supelco reformate sample was analysed in five consecutive injections in order to determine the repeatability of the system. Table 3 details the repeatability values as well as the reference values stated in method D8071. The repeatability of benzene, the system suitability sample is also detailed, however, no D8071 reference is specified.

Table 5. Repeatability of reformate sample (n=5)

	Mass %	SD	D8071 Ref
P	6.71	0.03	0.05-0.14
I	22.33	0.05	0.14-0.34
O	0.38	0.03	0.06-0.26
N	1.13	0.05	0.16
A	75.66	0.10	0.06-0.15
Benzene	6.08	0.01	

The values in Table 3 show excellent repeatability of the GC-VUV system, well within the specifications set in ASTM D8071. The excellent repeatability of benzene shows that the system was suitable for subsequent analyses.

CONCLUSION

The SCION GC with VUV detector offers the ideal solution for eliminating typical time consuming and difficult methods, when analysing spark ignition fuels for the determination of hydrocarbon classes and individual compounds. The PIONA+ analyser offers PIONA compound class characterisation in a single measurement whilst being operated to ASTM D8071 standards. Easy analysis of complex samples combined with automated data processing and confirmation via a spectral library, ensures a reliable performance with reproducible results in under 35 minutes.

SCION Instruments HQ
Livingston Business Centre,
Kirkton Road South, Livingston,
EH54 7FA, Scotland, UK.
Tel: +44 1506 300 200
sales-eu@scioninstruments.com
www.scioninstruments.com

SCION Instruments NL BV
4462, Goes,
Stanleyweg 4.
The Netherlands
Tel: +31 113 348 926
sales-eu@scioninstruments.com
www.scioninstruments.com