INSTRUMENTS BEYOND MEASURE

SCION INSTRUMENTS

Determination of Hydrocarbon Group Types by Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV)

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INTRODUCTION

The VUV detector is the next generation GC detector for PIONA analysis; simplifying the complex analysis of hydrocarbons 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, isoparaffins, olefin, napthenes and aromatics (PIONA) as well as other hydrocarbon classes to maintain the octane value of the system.

ASTM D6730 is the standard rest method for the determination of individual components in spark ignition fuels using GC-FID. However, 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, column 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 as a 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 compound content, in a single measurement. In addition, ASTM D8071 is the standard method for the determination of hydrocarbon group types using GC-VUV.

AIM

To demonstrate hydrocarbon group analysis of spark ignition fuels using GC-VUV.

EXPERIMENTAL

Instrumentation: SCION 436 GC with 8400 Autosampler and VUV detector
Software: VUV Analyze

Reference standards analysed included a PIONA+mix and an ASTM P-00800 calibration standard. Repeatability of the system was completed using a Supelco reformate sample. A gasoline sample was obtained and ran to specification of ASTM D8071 method.

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Table 1. Analytical conditions of the SCION 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

RESULTS

The retention indices (RI) and relative response factors (RRF) of all hydrocarbon classes and individual compounds were used during data processing. RRF of the classes and individual compounds are pre-programmed in the VUV Analyze software. 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 chemical structure of the compound. The built in UV spectral library was used to confirm peak identification. Spectral filters can be used to assist in discriminating between different compound classes with spectral filters applied post data acquisition to enhance analyte sensitivity. Baseline resolution is not vital when using the PIONA+ as the specific UV spectra still accurately identifies and quantifies compounds. Figure 1 demonstrates the separation achieved when analysing the ASTM P-00800 calibration standard by GC-VUV.

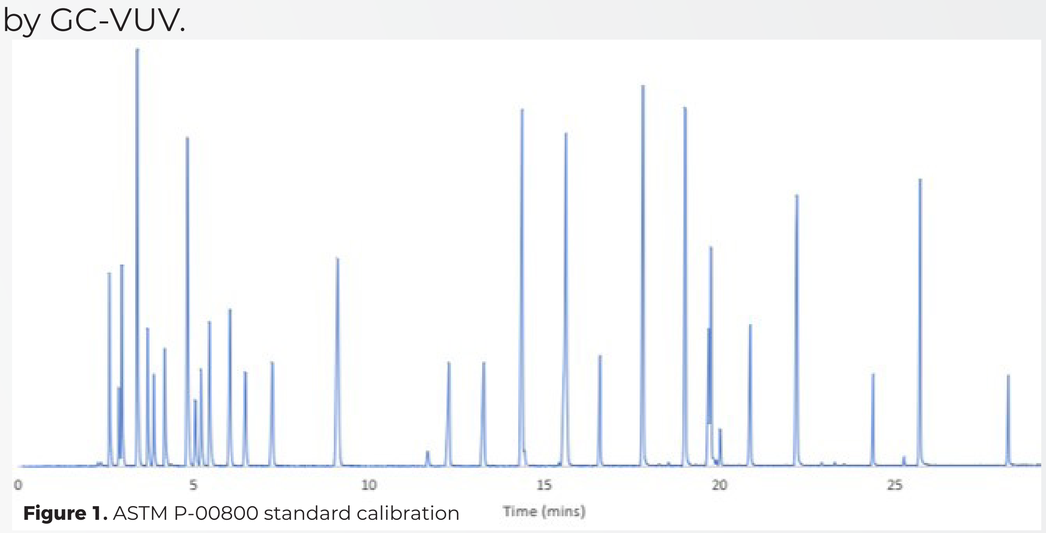

Figure 1. ASTM P-00800 standard calibration

Data processing is an automated process. The PIONA+ analyser divides the total chromatogram time region into individual time slices with each used to calculate the total absorbance. Both mass% and volume% are calculated from the total response contribution of each RRF. Figures 2 and 3 detail the comparison of the expected values and actual values of the ASTM calibration standard and PIONA mix results.

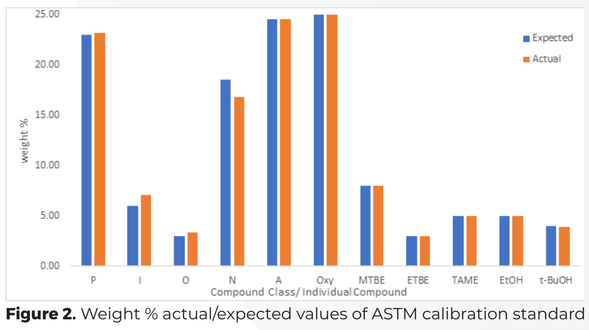

Figure 2. Weight % actual/expected values of ASTM calibration standard

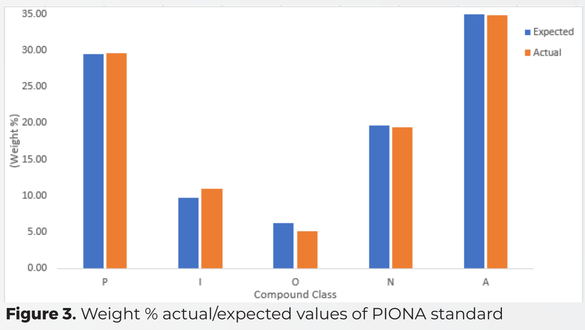

Figure 3. Weight % actual/expected values of PIONA standard

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 samples 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 specification limits stated in method D8071. The repeatability of benzene, the system suitability sample, is also detailed. However, no specification is detailed in the method. The values in Table 3 show excellent repeatability of the GC-VUV system, well within the specifications set in ASTM D8071.

Table 3. 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	

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 thirty-five minutes.