

Comparing ASTM D8071 (GC-VUV) & ASTM D6730 (DHA) for Hydrocarbon Analysis

Application Note

AN0025

INTRODUCTION

There are many challenges within the petrochemical industry and associated GC analysis methods, for the analysis of hydrocarbons in spark ignition fuels. 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, naphthenes 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.

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.

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.

This application note compares the data from VUV and DHA when the same samples are analysed using both analytical methods. The samples analysed included gasoline, alkylate and a racing fuel sample, on a SCION 436 GC, with respective detectors (VUV for ASTM D8071 and FID for D6730).

EXPERIMENTAL

The SCION 436 GC equipped with a 8400 autosampler, S/SL injector and VUV detector was used for the analysis of samples according to ASTM D8071 whereas the SCION 436 GC with a 8400 autosampler, S/SL injector and FID was used for DHA under ASTM D6730 specification.

Table 1 details the analytical parameters of the GC-VUV with Table 2 details the analytical parameters of the GC-FID.

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

Table 2. Analytical conditions of the GC-FID

Conditions	
S/SL	250°C, split 150:1
Column	100m x 0.25mm x 0.50µm
Oven Programme	5°C (hold 10 min), 5°C/min to 48°C (59mins), 1.3 °C/min to 200°C (5 mins)
FID	250°C

System suitability was performed following ASTM D8071 procedures.

RESULTS

Both DHA analysis and VUV analysis uses the retention indices and relative response factors (RRFs) of all hydrocarbon classes and individual compounds for data processing.

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. Unlike with processing DHA data, the VUV software is not dependent on very precise retention time.

Precise retention time identification is paramount to accurately identifying compounds in DHA. Additionally, VUV uses a built in UV spectral library for peak identification confirmation. The built in UV spectral library was used to confirm correct peak identification.

The following figures (1-5) show comparative data obtained when various samples were analysed by both VUV and DHA methods.

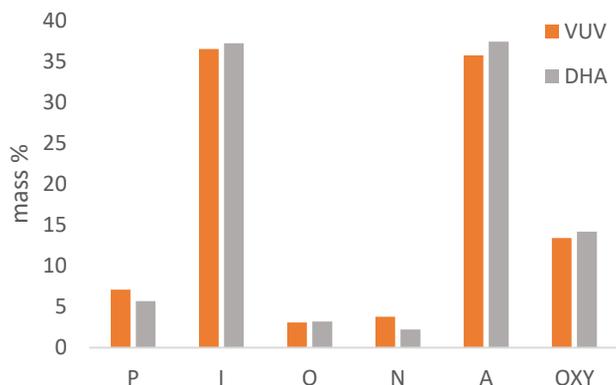


Fig 1. Data comparison of VUV and DHA analysis of a gasoline sample

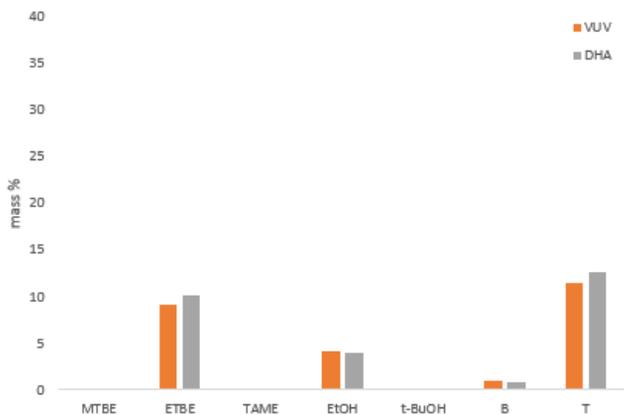


Fig 2. Individual component comparison of a gasoline sample

The above results show minimal variance between the total hydrocarbon groups mass % and individual mass % of a gasoline sample when analysed by both VUV and DHA systems. Figure 3 details that the paraffins, olefins, aromatics and oxygenates have highly similar results. However, there is a slight difference of 2% mass for isoparaffins and 3% difference for naphthenes. The difference in identification and quantitation could be due to manual peak assigning during DHA data processing. VUV uses a built in spectral library for peak identification, whereas DHA uses only retention indices and precise retention times, with manual data processing.

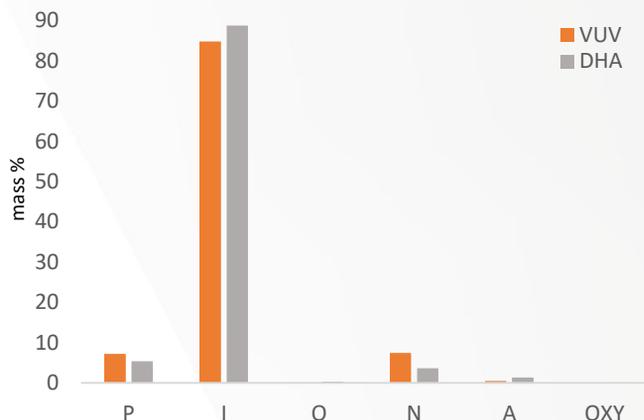


Fig 3. Alkylate comparison data of VUV and DHA analysis

The most important factor when analysing an alkylate sample is to identify the bulk composition which are the isoparaffins with the olefins and aromatics either at low levels or not contained within the sample at all. Figure 3 clearly shows that both VUV and DHA correctly identify the bulk composition of the alkylate sample.

Figure 4 details the comparison of results when a racing fuel was analysed on both VUV and DHA systems.

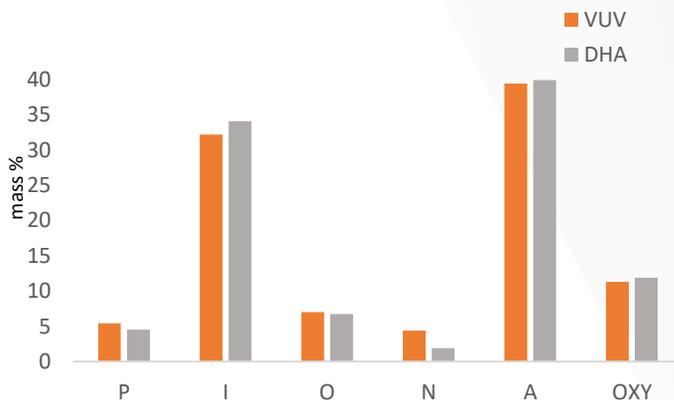


Fig 4. Racing fuel comparison data of VUV and DHA analysis

Although the VUV and DHA data shows a slight difference in naphthenes, the overall comparison shows highly similar results for all hydrocarbon classes. This is also reflected in the compound specific data, Figure 5. Most importantly, Figure 5 shows that the racing fuel sample did not contain MTBE, TAME, t-BuOH or butane, when analysed by both VUV and DHA.

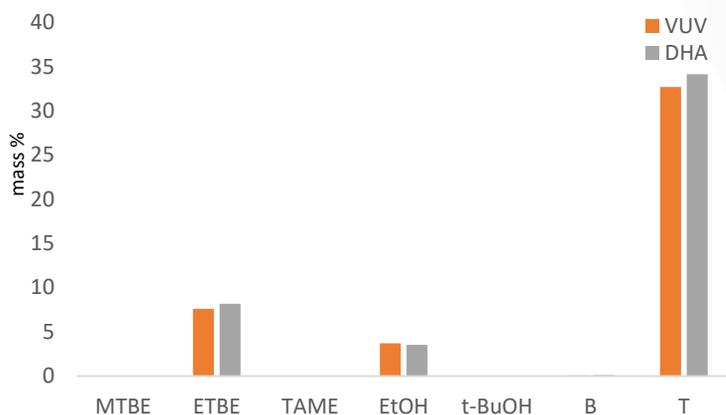


Fig 5. Individual component composition of racing fuel sample

CONCLUSION

Both DHA and VUV gave highly comparable results when the analysis of the same samples were performed on both systems. However, the SCION GC with VUV detector offers the ideal alternative solution to the time consuming DHA ASTM D6730 method; when analysing spark ignition fuels for the determination of hydrocarbon classes and individual compounds.