



EVOLUTIONARY DHA OR REVOLUTIONARY VHA? THE CHOICE IS YOURS!

In the early 1980s, one of my first experiences of GC analysis in the petroleum industry involved the detailed hydrocarbon analysis (DHA) of crude oil assay distillate fractions. Fused silica capillary columns were still in their infancy and, in order to achieve the best resolution available at that time, an in-house drawn and coated 100m glass capillary column with an OV1 stationary phase was employed with an optimised long and slow temperature programme and a flame ionisation detector (FID). Peak identification and assignments were accomplished by visually comparing the obtained chromatogram to a circa 2m long annotated reference chart recorder trace laid out on a lab bench. Peak areas from the integrator output were then assigned manually to the identified peaks and the results reported in tabular form. This was a slow and very labour-intensive process - so what has changed?

Nearly forty years later it would be expected to have seen great advances in DHA but on reviewing the current ASTM and related DHA methods, as summarised in Table 1, it is apparent that developments have been evolutionary rather than revolutionary.

These largely incremental developments have been primarily enabled by improved electronics and computerised automation and control in GC hardware, data collection, analysis and reporting. The continued development of fused silica capillary column technology has improved chromatographic resolution, but the ASTM methods listed in Table 1 have stated limitations in their scope due to incomplete resolution of important components.

In any analysis of complex mixtures, the key aim is resolution of the components of interest to allow identification and quantification and for DHA analysis complete resolution of all the components is the holy grail.

Improving Resolution in GC methods

Many practitioners believe improving resolution in gas chromatography can only be achieved by improving the resolving power of the chromatographic separation either by optimising the column performance or temperature programme for single column methods or the use of multidimensional chromatography which significantly increases complexity. However, improved resolution of individual components in gas chromatography can be achieved by the optimum combination and selection of a range of other technical levers including: - sample preparation, selective sampling,

Table 1:- Summary features of current DHA Methods.

DHA GC Method	ASTM D6729	ASTM D6730	ASTM D6733	Fast DHA	ASTM D7900	ASTM D5134
Sample Scope	Spark Ignition Fuels/Oxygenate Blends				Stabilised Crude	Petroleum Naphthas
Column Length	100m	100m+5m	50m	40m	50m	50m
GC Detector	FID	FID	FID	FID	FID	FID
Conc Range (m/m)	0.01 -30%	0.01 - 30%	0.01-15%	0.01-30%	0.01- 30%	0.01-30%
Max Olefins Conc %	25%	25%	20%	20%	20%	20%
Max FBP	225°C	225°C	225°C	225°C	270°C	270°C
Analysis Time (min)	140	174	135-162	28	118	118

sample introduction, detector selection and data capture and analysis. All the DHA methods listed in Table 1 use an FID detector as it is simple, rugged and it has a predictable linear response for hydrocarbon molecules over a large dynamic range. However, the FID does have some drawbacks in that although the response is generally proportional to the mass of carbon present and was good for quantification it does not provide any information about the molecular structure and therefore the identity of the hydrocarbon component being detected.

In this article we discuss how employing a VUV spectroscopic detector and bespoke spectral data capture and analysis has revolutionised detailed hydrocarbon analysis by achieving complete component resolution resulting in improved accuracy, speed and ease of use for a wide range of petroleum samples and applications.

The Power of Vacuum Ultraviolet Spectroscopy for Detailed Hydrocarbon Analysis

Molecular spectroscopy techniques such as NMR, FTIR, and UV/Vis have long been routinely employed in laboratories but Vacuum Ultraviolet Spectroscopy (VUV) has only been readily available since 2014 with the introduction by VUV Analytics of the first bench-top spectrometer capable of capturing the full VUV spectrum. In addition, unlike most other spectroscopic techniques, VUV works in the gas phase and is therefore ideal as an affordable detector for gas chromatography. Nearly all compounds absorb in the VUV region of the electromagnetic spectrum as the high energy, short wavelength VUV photons probe electronic transitions in the chemical bonds resulting in spectral "fingerprints" that are specific to individual compounds and can be readily identified by

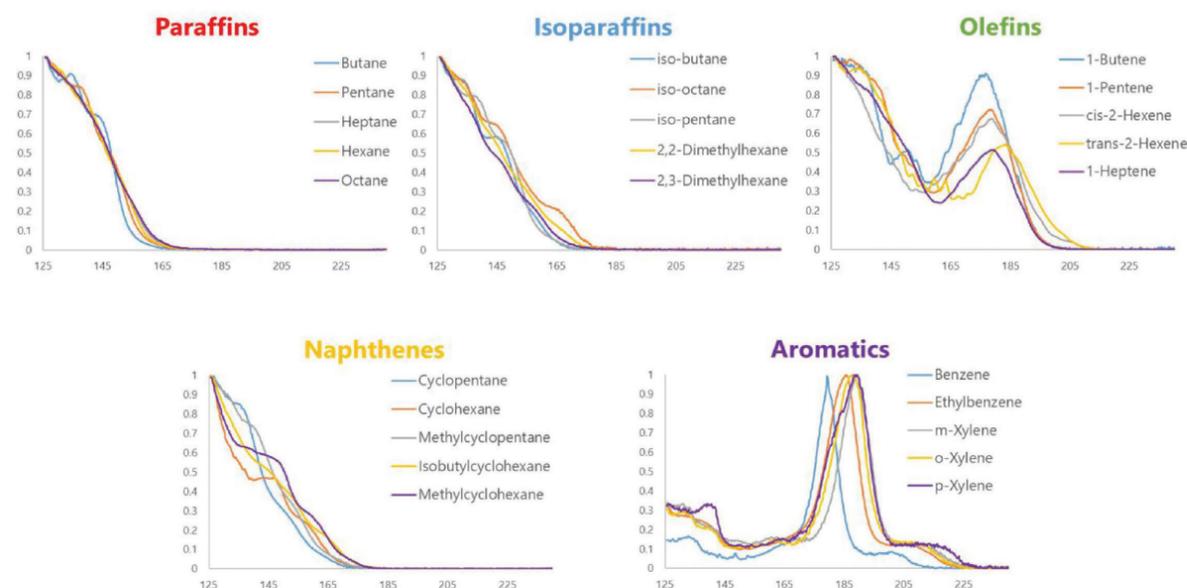


Figure 1 Example VUV Spectra showing unique compound specific and hydrocarbon class similarities for a selection of common molecules encountered in DHA applications

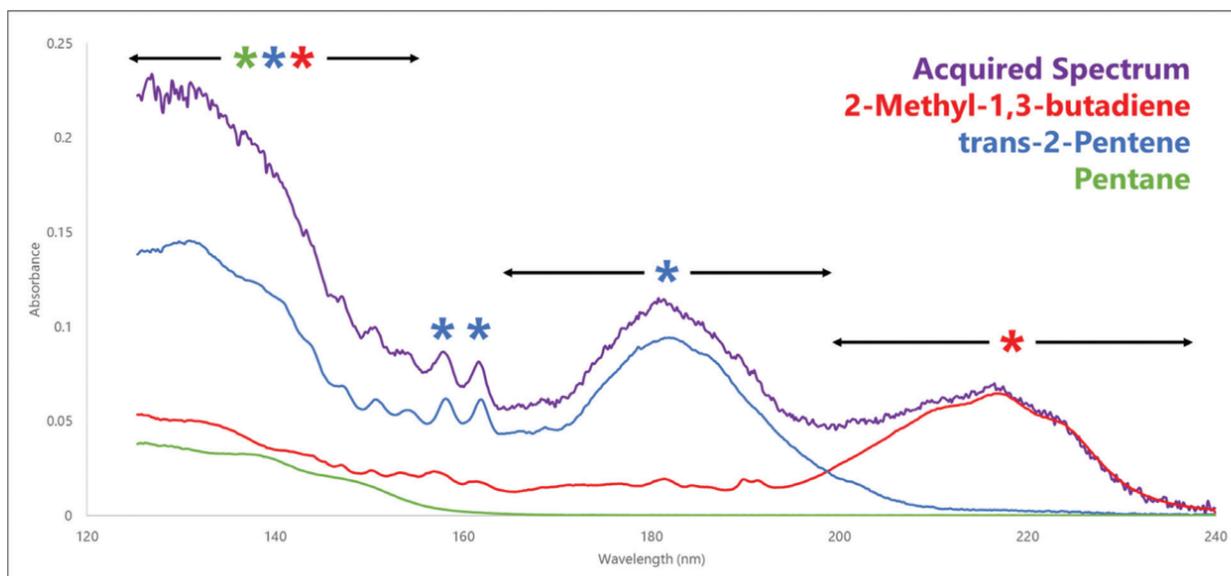


Figure 2 Illustration of a three-component spectral deconvolution of a single chromatographic peak

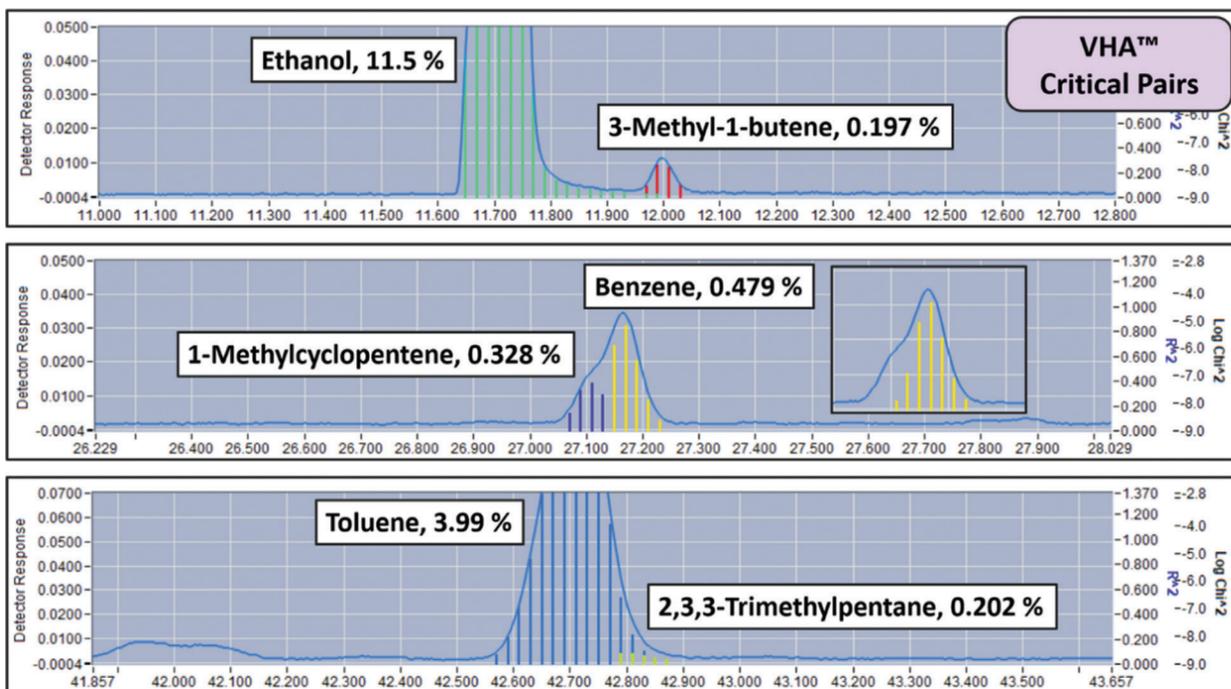


Figure 3 shows three examples of employing VUV spectroscopy to resolve critical pairs which are co-eluting components regularly encountered in conventional in DHA methods.

the VUV spectral library. Examples of the gas phase VUV spectra for different hydrocarbon class types shown in Figure 1. clearly illustrate that individual components have unique spectra which provide excellent selectivity and unambiguous identification and demonstrates the class similarities that make hydrocarbon type classification a simple process.

This approach differs significantly from traditional GC based DHA analysis where peaks and components are largely identified by retention time/index comparison to standard mixtures. With VUV detection the collection of unique spectra for every peak means that they can be examined for spectral purity using the bespoke VUV Analyze™ Software and either validated as a pure component or further analysed to deconvolute and identify co-eluting components. This is illustrated in Figure 2 and Figure 3 where examples of resolving and identifying co-eluting compounds

through unique VUV Time Interval Deconvolution™ (TID) spectral data analysis software are shown. Figure 2 shows the acquired spectra for a chromatographic peak overlaid with the deconvoluted spectra of the 3 components coeluting in that peak. These unique VUV spectra enable clear differentiation and quantification of closely related compounds such as structural isomers which makes VUV Spectroscopy coupled with GC a powerful and unique tool which is revolutionising DHA. In fact, it has been proposed that because the added spectral analysis adds verification to the results obtained that the VUV approach should be named Verified Hydrocarbon Analysis (VHA) to clearly differentiate it from conventional approaches to DHA and reflect the improved performance achieved using VUV spectroscopy.

The Added Value of Verified Hydrocarbon Analysis over Detailed Hydrocarbon Analysis

A summary comparison of key features of the VHA method with the ASTM D6730 DHA method is shown in Table 2 highlighting some significant differences and there are several reasons why those who currently run DHA methods with FID detection should seriously consider switching to the VHA method. In this section, we explore these differences in more detail.

Spectral Hydrocarbon Class Assignment

One trait of VUV spectra is that they share class similarities as shown by the hydrocarbon classifications illustrated in Figure 1. For example, each aromatic compound will have a unique spectrum which allows them to be identified individually but in addition as a class of compounds their spectra share similar shapes. As a result, these compounds can be classed automatically by the spectral analysis software which is not possible with DHA. Additionally, new and client custom compounds can be added to the VHA library as required ensuring that these compounds will be accurately identified in an ongoing fashion. VHA uniquely provides verified class-based reporting and individual speciation.

Improved Accuracy and Validation through Spectral Detection and Analysis

The Vacuum Ultraviolet range of the electromagnetic spectrum is adsorbed by nearly every compound, except for Argon and the common carrier gases Hydrogen and Helium, and as such it can be classed as a universal detector for gas chromatography. In addition, due to the collection of unique, compound specific spectra the detector could also be classed as a selective detector which makes the VUV detector unique amongst commonly used GC detectors.

Traditional DHA is limited by using an FID which generates two-dimensional data and therefore retention time is the sole means of peak identification which in turn means all compounds of interest must be resolved chromatographically to allow verified identification and quantification.

VHA by contrast acquires data in three dimensions and in addition to its retention time each compound has a unique spectral fingerprint that is used to identify the compound accurately every time. Thanks to this additional spectral validation unidentified compounds are typically less than 1% with VHA whereas with DHA the number flagged as unidentified often exceeds 15%.

This is clearly illustrated in Table 3 where hydrocarbon class data obtained by both VHA and DHA for two Naphtha samples and two Pygas samples is shown and in three cases DHA shows a >15% of the sample is not classified.

The results clearly show the benefits of the spectral analysis with improved identification and quantification of aromatics and olefins for the Pygas samples and of the valuable naphthene and isoparaffin content for naphthas. In addition as baseline resolution

Table 2: Summary comparison of key features of the VHA method with ASTM D6730 DHA

Method	GC Run Time	Column Length	Tuning Column	Data Processing	Data Review	Result Verification
DHA - ASTM D6730 GC-FID	174 min	100m	yes (5m)	Automated	Manual	Retention Time
VHA - VUV Analyser Platform GC-VUV	50 min	60m	no	Automated	Automated	Spectral Validation

Table 3: Comparison Hydrocarbon Class Analysis by VHA and DHA for Naphtha and Pygas Samples

Sample	Naphtha 1		Naphtha 2		Pygas 1		Pygas 2	
	VHA	DHA	VHA	DHA	VHA	DHA	VHA	DHA
Hydrocarbon Type								
Paraffin	21.0	19.1	23.2	22.0	3.6	3.8	0.4	0.5
Isoparaffin	31.4	27.6	31.5	25.4	4.1	4.6	1.3	2.0
Olefin	0.2	0.9	0.2	0.8	15.0	16.0	23.6	18.0
Naphthene	32.9	19.3	33.2	23.0	6.7	5.6	0.5	0.5
Aromatic	14.5	15.2	11.9	13.3	70.6	66.2	74.4	60.3
Total % Classified	100.0	82.1	100.0	84.5	100.0	96.1	100.074	81.3

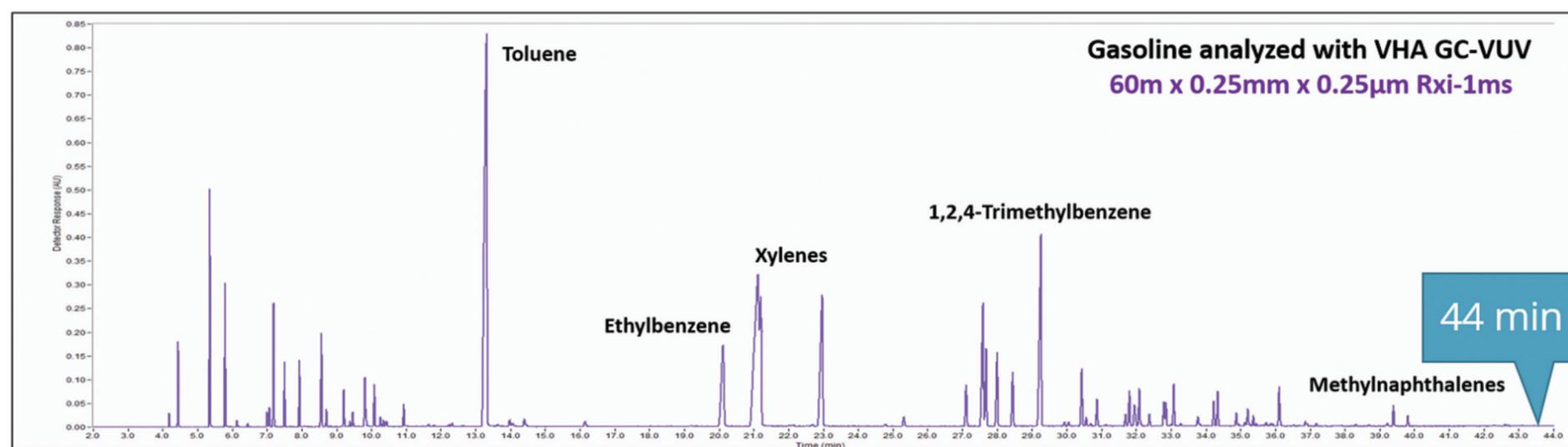
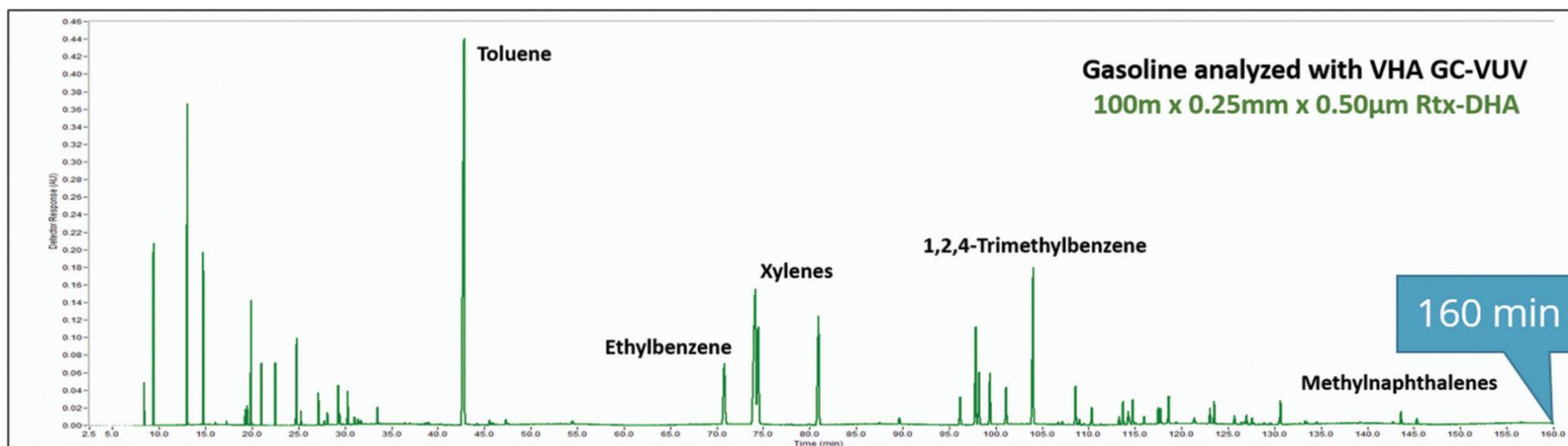


Figure 4. A gasoline sample run under ASTM D6730 GC conditions (top) and VHA conditions. The VHA run maintains nearly the same chromatography in less than one third of the D6730 run time.

is not an issue for VHA the so called "Critical Pairs" (a common issue with DHA that requires the use of a tuning column) are easily deconvolved in the VUV Analyze Software thanks to TID™ which works by slicing a chromatogram into regularly spaced time intervals, each with a unique summed absorbance spectrum. Each slice is then automatically analysed to determine the contribution of each compound to the measured spectra. This means complex chromatograms can be easily, reliably, and accurately deconvolved and analysed, without the need for a fixed peak table.

Speed of Analysis and Reporting

A complete VHA analysis plus data processing only takes 50 minutes compared to 2 to 3 hours plus of the other high resolution DHA methods listed in Table 1. The added selectivity and ability to resolve coeluting compounds of the VUV detector allows the use of a shorter column than DHA allowing faster instrumental run times as illustrated for gasoline analysis in Figure 4.

In addition to a faster chromatographic run time the data processing, analysis and spectral validation is fully automated and, unlike DHA with FID, there is no need for manual data review and validation which can be very complicated, time consuming and costly in terms of experienced staff effort.

Ease of Use

VHA is fully automated - Simply run the analysis method and the VUV Analyze Software handles the rest. Unlike other techniques that require complicated sample preparation, VHA operators simply fill the appropriate vial with the sample, load it in the autosampler and press go. In addition, VHA is a simple single column method which does not require a precolumn and therefore eliminates the need for column tuning. Turning to data analysis, component identification is fully automated and, unlike DHA, there is no need for complicated manual data review. Another advantage of VHA is

it is calibration free as the component spectra do not change and the molar absorption coefficient at any wavelength is an intrinsic property of the species. This, together with peak deconvolution and spectral identification, allows the Beer-Lambert Law to be applied for quantification removing the need for a fixed peak table. (Note: this does not mean that users should not run check standards and should always follow protocols as specified in their laboratory quality procedures.)

A Flexible Platform for Many Applications

The VHA method runs on the VUV Analyzer™ Platform which has been developed with value, ease-of-use, and flexibility in mind. It is apparent in Table 1 that different sample types require different DHA instrumental set ups but VHA on the VUV Analyzer can be applied to a wide range of sample types including: - Gasolines, Naphtha, Reformate, Alkylate, PyGas, FCC gasoline and LPG.

In addition, users can seamlessly transition from VHA to jet fuels analysis, to finished gasolines, or even diesel fuel without the need to change hardware or setup. This means using the same GC, VUV detector, and software for all analysis. This ultimately revolutionizes hydrocarbon analysis across the board by delivering improved accuracy, reduced operator complexity, accelerated analysis times and superior data quality and consistency.

Summary Comments and Conclusions

For almost sixty years single column GC with FID has been the dominant technique for the quantitative analysis of hydrocarbon mixtures and during this time the approach has evolved mainly through improved hardware, automation and computerised data processing technology. However, the limitations of the FID detector have meant that this evolution has not yet managed to achieve the holy grail of complete resolution and identification of every component in the range of complex hydrocarbon mixtures

Gasoline analyzed with VHA GC-VUV
100m x 0.25mm x 0.50µm Rtx-DHA

160 min

Gasoline analyzed with VHA GC-VUV
60m x 0.25mm x 0.25µm Rxi-1ms

44 min

encountered in everyday use.

The evolution of GC-FID has now been threatened with extinction by a revolution in GC detector technology by the development of the VUV gas phase detector. It is that very rare beast in that it is both a universal and a selective GC detector which, due to the unique compound specific spectra obtained combined with common spectral features for hydrocarbon classes, allows hydrocarbon type identification, verification and quantification in a way which has previously not been possible.

Since its introduction in 2014 the application space of the VUV detector for GC has grown so much that the company now provides a dedicated VUV Analyzer™ Platform for hydrocarbons capable of providing a range of analyses which comply with ASTM standard methods. Gaining approval for so many standard methods in such a short time is a testament to the power and applicability of the technique and a clear indication that we are witnessing a revolution in GC detector technology with the VUV. The latest addition to the suite of applications tackles the issues and failures commonly encountered in DHA (Detailed Hydrocarbon Analysis) methods and offers such an improvement in terms of verified accuracy, speed of analysis and ease of use that it deserves differentiation from other methods and the name Verified Hydrocarbon Analysis (VHA) has been used throughout this article.

The indication is that the VUV revolution will continue to bring new insights to GC analysis in the near future and will become an increasingly powerful tool, not only in the hydrocarbon based industries, but in any industry where the analysis of components in complex mixtures cannot be verified by chromatographic resolution alone.

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