

Vacuum Ultraviolet Detection for Gas Chromatography: A Powerful Tool for Petrochemical Analysis

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Gas chromatography has been a mainstay of analytical measurement techniques in the petrochemical industry since the 1950s and 1960s [1]. Fossil fuels, ranging from natural gas to crude oil, serve as feedstocks for the production of a variety of, among others, high value volatile and semi-volatile fuels and chemical building blocks for materials. Distillates and catalytic conversion products need to be carefully characterised to predict their performance and determine their quality; in many cases, gas chromatography (GC) is the most reasonable choice for analysis.

A cadre of GC detectors to characterise high efficiency separations have become well established. Of them, the mass spectrometer detector (MS) has arguably been the most impactful given its capability for qualitative and quantitative analysis. Very few other detectors provide any qualitative information. This reality, and the complexity of many sample types, have also driven a long history in chromatographic stationary phase development. Many would like to debate whether such an extensive history and established use for GC points to a mature technique where little room for innovation remains; however, continued and recent developments in technologies such as ionic liquid stationary phases and in comprehensive multidimensional separations paints a different picture.

Vacuum Ultraviolet Spectroscopic Detection

Another recent and impactful GC development was the introduction of the vacuum ultraviolet spectroscopic absorption detector (VUV) [2,3]. Prior to 2014, when the detector was commercialised, absorption measurements in the vacuum ultraviolet regime (< 180 nm) were largely relegated to bright source synchrotron facilities. As illustrated in Figure 1, through the use of a deuterium lamp, reflective optics, and a charge-coupled device, a benchtop VUV system is now available to simultaneously measure full range absorption (like a traditional photodiode array detector) from 120 – 240 nm at a rate of up to 100 Hz. Virtually all chemical species absorb light in this wavelength range and have unique

gas phase absorption spectra. Luckily, GC carrier gases have relatively low absorptivity compared to most analytes desired to be analysed. Concentration-dependent absorption follows the Beer-Lambert Law for this mass-sensitive detector. Thus, the VUV, like the MS, is a GC detector that has capabilities for both qualitative and quantitative analysis.

Petrochemical mixtures are synonymous with the presence of both saturated and unsaturated hydrocarbons. Modern analytical chemists would largely consider such systems to be incompatible with electron absorption spectral analysis, except where aromatic and conjugated compounds are present. However, photons in the vacuum ultraviolet wavelength region possess sufficient energy to probe even alkanes, which absorb fairly strongly in the range of 120 – 160 nm, due to $\sigma \rightarrow \sigma^*$ transitions. Further, the energies associated with transitions between highest

occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are highly dependent on molecular structure. Even very small changes in molecular structure (e.g., for various different isomers) create significant changes in the shape of absorption spectra. With approximately 0.5 nm resolution and highly reproducible spectral features, even minor differences in spectra can be discerned. The ability to distinguish isomers using the VUV detector is probably one of its most advantageous features; this gives it a high degree of complementarity to MS, which can have trouble distinguishing some isobaric species, even after ion fragmentation.

Much like modern electron ionisation MS, VUV relies heavily on the registration of pure absorption spectra in a library for qualitative analysis. There are currently more than 2000 compounds in the VUV library, which is quite sufficient for many mainstream applications,

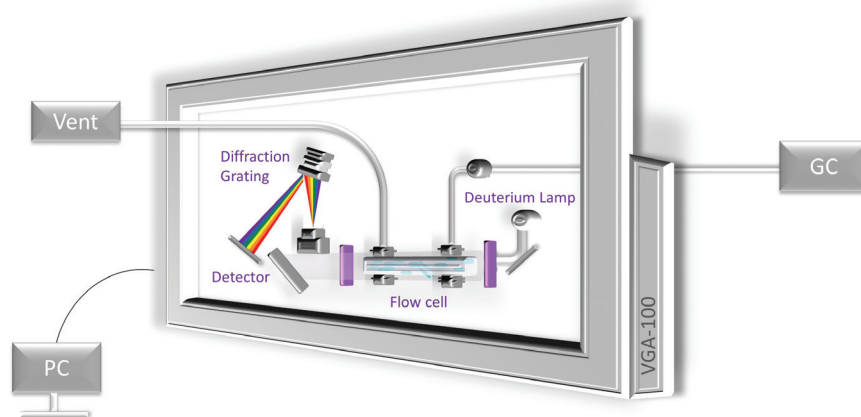


Figure 1: Generalised schematic of the VUV detector (VGA-100) from VUV Analytics, Inc.

but this number is also growing rapidly as new adopters contribute additional applications and compound spectra.

Figure 2 shows some examples of overlaid petrochemical species of interest. Ratios of phytane (2,6,10,14-tetramethylhexadecane, $C_{20}H_{42}$) to C18 (n-octadecane, $C_{18}H_{38}$) can be used to identify the source and monitor the degree of weathering of diesel fuels introduced into the environment [4]. From a VUV spectroscopy viewpoint, Figure 2A demonstrates the spectral difference between a linear and branched saturated hydrocarbon. This is a significant difference and means for quantifying such differences based on sum-squared-residuals of pairwise compared spectra have been published previously for a variety of applications [5-8]. Nevertheless, for the large range of linear, branched, and cyclic saturated hydrocarbons that occur in petrochemical mixtures, GC separations are still essential for fully resolving homologous series of compounds. For example, the VUV/UV absorption spectra for n-C8 and n-C9 alkanes would be largely indistinguishable, but these can be readily separated by GC.

Some isomeric species are very challenging to separate by GC. Figures 2B and 2C show VUV absorption spectra for the three xylene isomers and three selected dimethylnaphthalene isomers, respectively. These aromatic compounds are strong chromophores (the absorptivity of benzene at 180 nm is about 10,000 times higher than at 254 nm), and they are highly responsive to the VUV detector (low picogram (pg) on-column detection limits). Also, as expected, the strong absorption features associated with the $\pi \rightarrow \pi^*$ transitions in aromatic compounds are at longer wavelengths (lower energies) compared to the spectral features observed for saturated compounds. Whereas electron ionisation mass spectra for each of the xylene and dimethylnaphthalene sets are virtually indistinguishable, their VUV spectra are very different. Not shown, but also highly distinguishable, are cis-/trans-isomers of olefins and fatty acids [9].

Deconvolution

Another key advantage of VUV detection is the ability to easily deconvolve coeluting analytes. When two or more analytes enter the flow cell at the same time, the observed absorption signal is the sum of the absorption for each of the individual compounds. The instrument software has been designed such that when coelution is apparent or suspected, weighted linear

combinations of reference library spectra can be used to determine the contribution of individual species to a peak or peaks containing multiple analytes. Figure 3 demonstrates this concept. For the measurement of oxygenates in gasoline, a coelution was detected, the combined spectra for which is shown in grey in Figure 3A. Overlaid with these combined spectra are the normalised reference spectra for the two components, ethanol and t-butanol, which were determined to have contributed to the coelution. The measured and deconvolved chromatograms are then shown in Figure 3B. In this case, t-butanol eluted before ethanol, because a polar ionic liquid stationary phase was used for the analysis.

The ability to deconvolve two coeluting compounds, which are present in varying degrees of abundance does ultimately depend on the spectral similarity of the analytes. We have studied this concept quite extensively. As was shown in Figure 2C, dimethylnaphthalene isomers have fairly similar spectra, and there are many isomer combinations for this class of compounds that are prone to coelute on most GC stationary phases. We systematically studied the range of relative abundance over which the coelutions of the dimethylnaphthalenes could be reliably deconvolved [5]. It was shown that if one of the isomers was present at reasonable quantity (nanogram (ng) on-column), that a coeluting isomer could still be reliably deconvolved when it was present in two orders of magnitude lower abundance. That level of performance is of practical utility for real world samples.

In other studies, we examined the coelution of simple carbohydrates [7], and even deuterium-labelled isotopologues of various analytes [8]. In those cases, spectral similarity

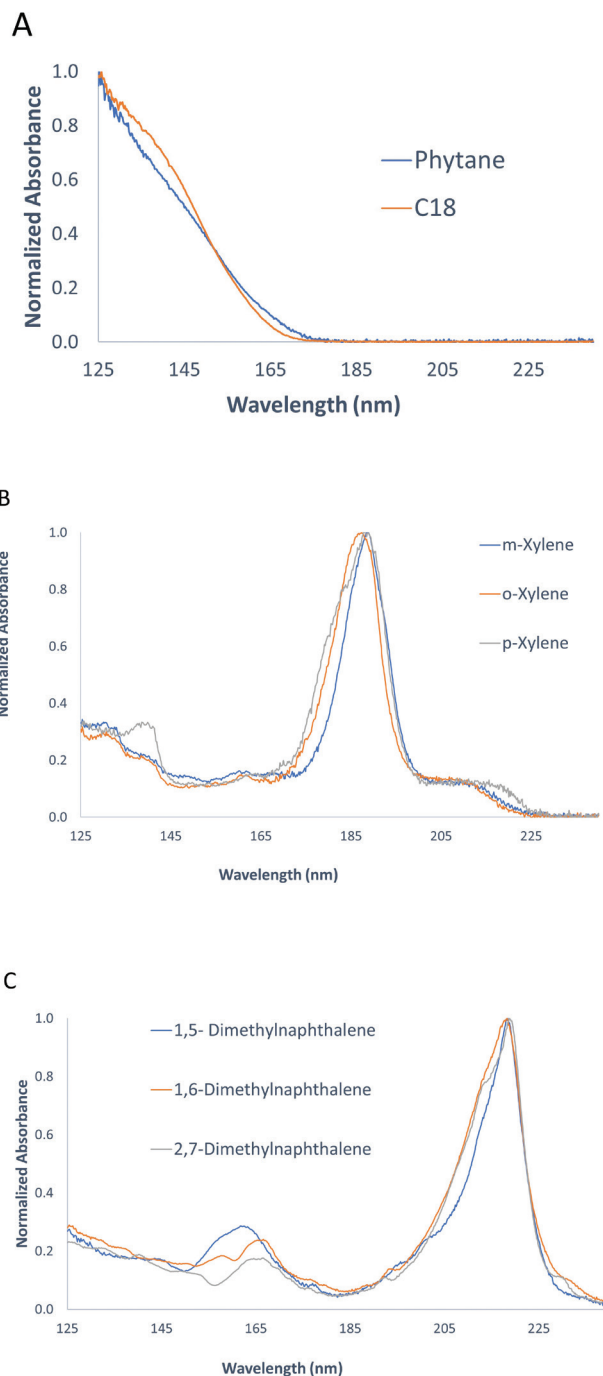


Figure 2: Spectral overlays to show spectral differences for A) branched and linear alkanes, B) xylene isomers, and C) dimethylnaphthalene isomers.

was very high and it was judged that a much lower range of relative abundances between two compounds could be deconvolved. Those are perhaps worst-case scenarios. When two analytes of different compound classes coelute, they will generally have very dissimilar spectra. In those cases, a component that is more than three orders of magnitude lower in abundance than a high abundance compound could likely be reliably deconvolved from one another. Of course, it is required that the lowest abundance compound still be present above its detection limit.

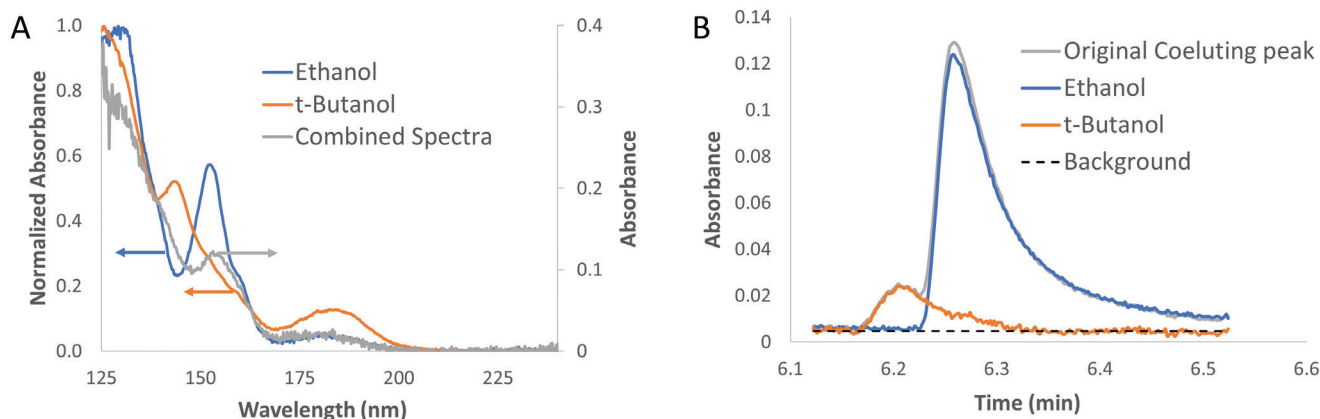


Figure 3: Deconvolution of the coelution of gasoline oxygenates: A) shows the combined observed spectrum and the normalised spectra for the individual compounds, while B) shows the combined observed chromatogram and the deconvolved individual contributions of each compound to the total signal.

Time Interval Deconvolution

Building off the concept of deconvolution, it became apparent that it was not necessary to consider deconvolution of coeluting compounds peak-by-peak. A new concept called time interval deconvolution (TID) was introduced, whereby an entire chromatogram can be divided into discrete time intervals, and then the absorption of compounds in each time interval could be determined. The contributions throughout the chromatogram could then be combined or binned according to desired species or classes of compounds to characterise the composition of the mixture. This is demonstrated schematically in Figure 4 for a small snap-shot of the separation of a gasoline sample.

One way that finished gasoline is characterised is based on its paraffin (linear alkane), isoparaffin (branched alkane), olefin, naphthene (cyclic alkane), and aromatic (PIONA) content. Because the VUV spectra for compounds are highly class specific, the PIONA classification of fuels was a natural application, and the concept of TID allows it to be performed in a rapid automated fashion. The details of this approach for finished gasoline is described in the literature [10], and recently an ASTM method (D8071) [11] was approved for PIONA analysis of fuels based on the TID concept. We also demonstrated how TID could be used for the speciation of industrial Aroclor mixtures of polychlorinated biphenyl compounds [12]. Samples that can be well characterised in terms of their content would be highly amenable for further application of TID. Realistically, such a treatment removes the need for traditional peak integration approaches.

Other Applications and Future Work

Other groups besides ours have shown that the VUV detector is useful for the characterisation of different fuels, especially in combination with the aforementioned use of ionic liquid stationary phases [13] and comprehensive multidimensional separations [14,15]. Its application to some higher fuels will rely on the further development of the library to incorporate more higher molecular weight hydrocarbons, or other means to characterise spectra measured for compounds that may not be available to measure separately and enter into the library.

A newer generation VUV detector has been recently introduced, which features a wider absorbance wavelength range (120 - 430 nm), higher operating temperature (430°C), and increased sensitivity. This should further expand the application base to higher distillate products, for which much more limited characterisation techniques are currently available. As the application base of the VUV detector for GC continues to grow, its value to researchers in a variety of research fields will be realised; however, its applications in the petrochemical industry has already demonstrated its usefulness and high degree of complementarity to other available detection techniques, especially MS.

Disclaimer: KAS is a member of the Scientific Advisory Board for VUV Analytics, Inc.

References

1. Bartle, K.D.; Myers, P. History of Gas Chromatography. *Trends Anal. Chem.* 2002, 21, 547-557.

2. Schug, K.A.; Sawicki, I.; Carlton Jr., D.D.; Fan, H.; McNair, H.M.; Nimmo, J.P.; Kroll, P.; Smuts, J.; Walsh, P.; Harrison, D. Vacuum Ultraviolet Detector for Gas Chromatography. *Anal. Chem.* 2014, 86, 8329-8335.

3. Santos, I.C.; Schug, K.A. Recent advances and applications of gas chromatography vacuum ultraviolet spectroscopy. *J. Sep. Sci.* 2017, 40, 138-151.

4. Christensen, L.B.; Larson, T.H. Method of determining the age of diesel oil spills in the soil. *Ground Water Monit. Remediat.* 13 (1993) 142-149.

5. Schenk, J.; Mao, X.; Smuts, J.; Walsh, P.; Kroll, P.; Schug, K.A. Analysis and Deconvolution of Dimethylnaphthalene Isomers Using Gas Chromatography Vacuum Ultraviolet Spectroscopy and Theoretical Computations. *Anal. Chim. Acta* 2016, 945, 1-8.

6. Skultety, L.; Frycak, P.; Qiu, C.; Smuts, J.; Shear-Laude, L.; Lemr, K.; Mao, J.X.; Kroll, P.; Schug, K.A.; Szewczak, A.; Vaught, C.; Lurie, I.; Havlicek, V. Resolution of isomeric new designer stimulants using gas chromatography – vacuum ultraviolet spectroscopy and theoretical computations. *Anal. Chim. Acta* 2017, 971, 55-67.

7. Schenk, J.; Nagy, G.; Pohl, N.; Leghissa, A.; Smuts, J.; Schug, K.A. Identification and Deconvolution of Carbohydrates using Gas Chromatography-Vacuum Ultraviolet Spectroscopy. *J. Chromatogr. A* 2017, 1513, 210-221.

8. Weston, C.; Smuts, J.; Mao, J.X.; Schug, K.A. Investigation of Gas Phase Absorption Spectral Similarity for Stable-Isotopically Labeled Compounds in the 125 – 240 nm Wavelength Range. *Talanta* 2017 (In Press). <https://doi.org/10.1016/j.talanta.2017.09.033>

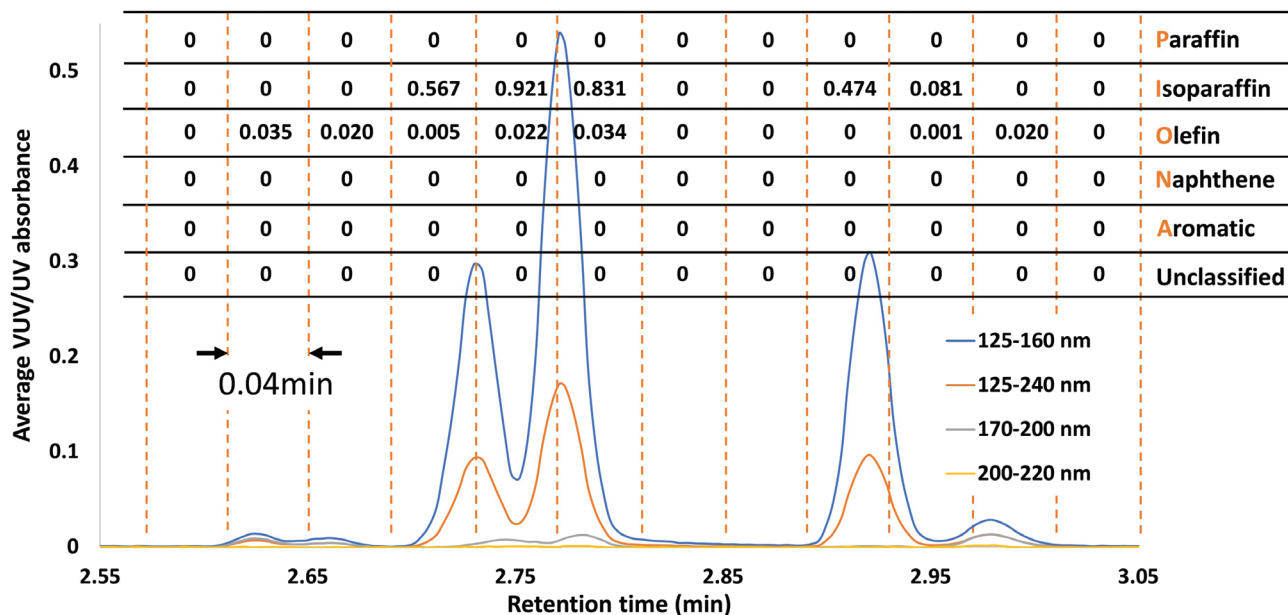


Figure 4. A representation of time interval deconvolution. A short portion of a gasoline sample chromatogram is shown divided into time intervals for which the absorption of PIONA class compounds is determined for each interval. This analysis can be performed rapidly and in an automated fashion across the entire chromatogram, and then relative response factors used for each class and species of interest to convert absorbance into the relative composition of each in the sample.

9. Fan, H.; Smuts, J.; Bai, L.; Walsh, P.; Armstrong, D.W.; Schug, K.A. Gas Chromatography – Vacuum Ultraviolet Spectroscopy for Analysis of Fatty Acid Methyl Esters. *Food Chem.* 2016, 194, 265-271.

10. Walsh, P.; Garbalena, M.; Schug, K.A. Rapid Analysis and Time Interval Deconvolution for Comprehensive Fuel Compound Group Classification and Speciation using Gas Chromatography – Vacuum Ultraviolet Spectroscopy. *Anal. Chem.* 2016, 88, 11130-11138.

11. ASTM D8071-17, Standard Test Method for Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive

Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV), ASTM International, West Conshohocken, PA, 2017, www.astm.org

12. Qiu, C.; Cochran, J.; Smuts, J.; Walsh, P.; Schug, K.A. Gas Chromatography-Vacuum Ultraviolet Detection for Classification and Speciation of Polychlorinated Biphenyls in Industrial Mixtures. *J. Chromatogr. A* 2017, 1490, 191-200.

13. Weber, B.M.; Walsh, P.; Harynuk, J.J. Determination of Hydrocarbon Group-Type of Diesel Fuels by Gas Chromatography with Vacuum Ultraviolet Detection. *Anal. Chem.* 2016, 88, 5809-5817.

14. Groeger, T.; Gruber, B.; Harrison, D.; Saraji-Bozorgzad, M.; Mthembu, M.; Sutherland, A.; Zimmermann, R. A Vacuum Ultraviolet Absorption Array Spectrometer as a Selective Detector for Comprehensive Two-Dimensional Gas Chromatography: Concept and First Results. *Anal. Chem.* 2016, 88, 3031-3039.

15. Zoccali, M.; Schug, K.A.; Walsh, P.; Smuts, J.; Mondello, L. Flow-Modulated Comprehensive Two-Dimensional Gas Chromatography Combined with a Vacuum Ultraviolet Detector for the Analysis of Complex Mixtures. *J. Chromatogr. A* 2017, 1497, 135-143.