

VUV PIONA+™ IMPROVES ACCURACY OF HYDROCARBON REPORTING IN GASOLINE

VUV Analytics, Inc. has demonstrated the ability to improve the accuracy of hydrocarbon compound characterisation in gasoline range samples using its VUV PIONA+™ product solution. Reporting errors often encountered in detailed hydrocarbon analysis (DHA) using flame ionization detection (FID), such as peak misidentification and unresolved co-elutions, can be overcome using VUV spectral matching and deconvolution. Additionally, VUV eliminates traditional DHA requirements for sub-ambient oven temperature programs and column pre-tuning.

VUV PIONA+™ utilises single-column gas chromatography (GC) combined with vacuum ultraviolet (VUV) spectroscopy to provide accurate compound speciation up to C6 and bulk compound class characterisation at higher carbon numbers. In addition, specific analytes throughout the chromatogram such as individual oxygenates or aromatics belonging to the BTEX complex can be speciated. The product solution combines a VGA-100, the world's first VUV absorption GC detector, with the automated software analysis of VUV Analyze™.

GC-VUV absorbance data is three dimensional (time, absorbance, wavelength) and specific to compound chemical structure. Chromatographic co-elution events common to DHA can be addressed using VUV spectral matching and software deconvolution. VUV absorbance spectra are typically highly structured and distinct for individual compounds, yet exhibit the intuitive property of having similar features when measuring related compound classes.

The VUV Analyze™ engine implements equations and fit procedures that result in deconvolution of absorbance spectra that contain contributions from multiple species, is capable of binning and storing response contributions from each deconvolution analysis, and reporting a combined total response at the end of the analysis. The data processing includes a database library of VUV reference spectra, compound class information, density, approximate retention index values, relative response factors for each hydrocarbon class, and relative response factors for individually reported compounds. Compound class or specific compound concentrations can be reported as mass or volume percent.

An example of a GC-VUV deconvolution important to hydrocarbon analysis can be seen in the zoomed-in GC-VUV chromatogram of Figure 1. The co-elution of benzene and 1-methylcyclopentene shown resulted from a gasoline sample run with a 100-meter column (100% poly(dimethyl siloxane) phase, 0.25mm ID, 0.5µm film thickness). Neither a tuned pre-column nor sub-ambient start temperature was used. VUV software deconvolution was performed during post-run analysis to achieve accurate quantitation of both compounds. A reconstructed chromatogram is overlaid to display the relative proportion of benzene and 1-methylcyclopentene in the co-eluting peak. Numerous other co-elution events in gasoline samples can be resolved using VUV PIONA+™. Figure 1 inset demonstrates how the unique spectral signatures of compounds in the VUV wavelength range (125 – 240 nm) enable identification and deconvolution of co-eluting analytes. The co-elution of toluene and 2,3,3-trimethylpentane is another chromatographic separation challenge commonly encountered

with hydrocarbon analysis methods. ASTM Method D6730 recommends tuning a 5% phenyl pre-column to provide better separation of these compounds. ASTM Method D6729 uses a sub-ambient temperature start to enhance separation of early eluting compounds, but only achieves separation of toluene and trimethylpentane for a limited range of concentrations. Figure 2 shows the deconvolution of toluene and 2,3,3-trimethylpentane by VUV Analyze™. Analyte spectral profiles are fit with VUV library spectra to provide the identities and relative concentrations of the co-eluting compounds. The spectral fits at the front and back of the co-elution are given at the bottom of the figure. The resolution

of these co-eluting compounds was accomplished using a 100-meter column (100% poly(dimethyl siloxane) phase, 0.25mm ID, 0.5µm film thickness) and deconvolution, with no sub-ambient start conditions or pre-column tuning.

Complete chromatographic separation of all analytes using either ASTM D6729 or ASTM D6730 is impossible. The result in the previous example is the potential over-reporting of toluene when a significant amount of 2,3,3-trimethylpentane is present. Even when sufficient separation of early eluting analytes is achieved, it is not possible to separate all of the later eluting compounds. Further over-reporting of aromatics can occur when the sample contains

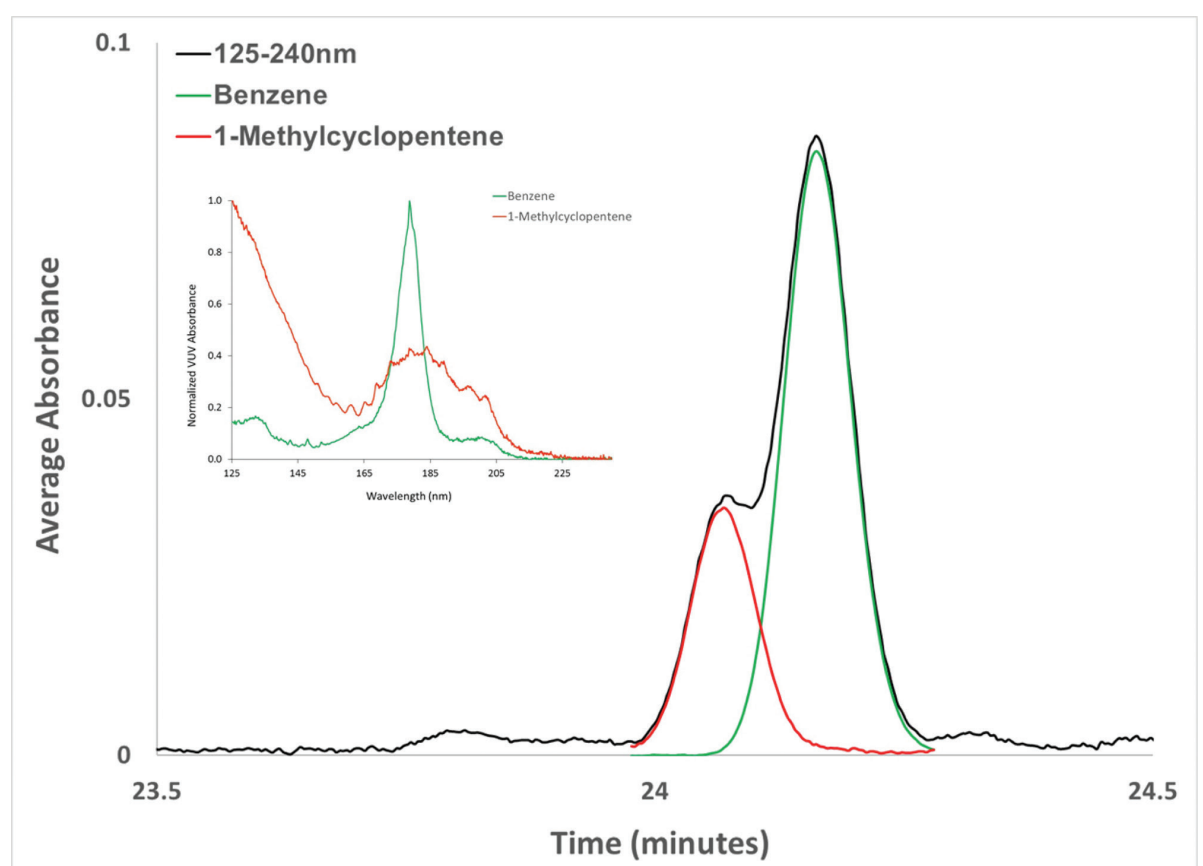


Figure 1: GC-VUV chromatogram of gasoline sample zoomed-in to show the co-elution of benzene and 1-methylcyclopentene. A chromatographic shoulder starting at 24 minutes is observed from the full range absorbance (125 – 240 nm) response. The deconvolution performed by VUV software during post-run analysis is overlaid to display the relative proportion of both compounds. The VUV Absorbance spectra of benzene and 1-methylcyclopentene are overlaid in the figure inset to demonstrate how their unique spectral profiles enable straightforward identification and deconvolution.

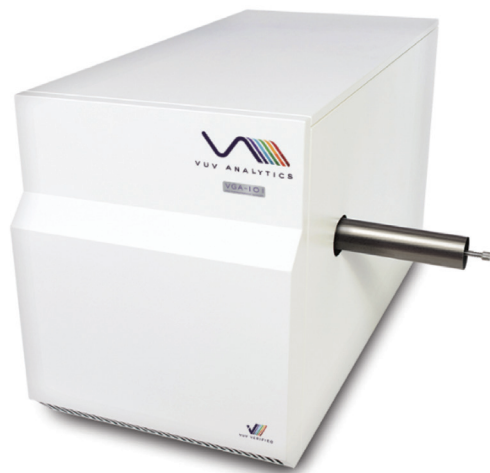
significant concentrations of higher boiling saturated hydrocarbon compounds. Figure 3 shows a GC-VUV chromatogram of a blended gasoline sample with substantial C10-C12 aromatic content. Spectral filters have been applied during post-run data analysis to highlight the relative amounts of aromatics (175-205nm, 125-160nm) and saturates (125-160nm) present in the sample. This example presents the ideal scenario for DHA in that aromatic peaks can be assigned via peak detection and retention time matching, and integrated with relative accuracy.

The application of DHA becomes significantly more difficult when gasoline samples have significant concentrations of both C10-C12 aromatics and saturates. The noticeable difference in chromatographic profiles can be seen in Figure 4. The 125-160nm spectral filter shows substantial saturate response between and overlapping with aromatic peaks. Determining the amount of response attributable to aromatics and saturates in this type of sample using a detector capable of only response and retention time output is very difficult, even when the aromatic peaks are correctly identified. Dropping vertical integration lines attributes too much response to aromatics. Depending on how poorly resolved the saturate response is, some of it may be skipped over, treated as background, or mislabelled. In either case, there is potential of over-reporting aromatic concentration and under-reporting saturated hydrocarbon content. The impact of this type of error could be especially significant in the case of heavy naphthas, where particularly high concentrations of C10 – C12 saturates elute with similar boiling range aromatics. Increasing the GC runtime or employing tuned pre-columns could help improve the chromatographic separation, but the sheer number of saturated hydrocarbon species in this carbon range means these tactics will not fully resolve the aromatic and saturate overlap. Other techniques utilising complex multidimensional chromatography can separate hydrocarbon classes well but offer limited speciation of individual compounds.

VUV PIONA+™ delivers a more accurate, reproducible alternative for characterizing hydrocarbon content in complex gasoline samples. Co-elution and unresolved chromatography is addressed through the use VUV spectral matching and software deconvolution. Figure 5 demonstrates how VUV Analyze™ performs time interval deconvolution¹ (TID) to determine the contribution of analyte classes to the total absorbance response within each time slice interval of co-elution events. This analysis methodology was applied to the blended gasoline example with significant aromatic and saturated hydrocarbon chromatographic overlap in the C10 – C12 region of the sample. The software reports both compound types according to their PIONA classification in the bulk analysis that includes carbon number and mass % composition.

References

1. P. Walsh, M. Garbalena, K.A. Schug, 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
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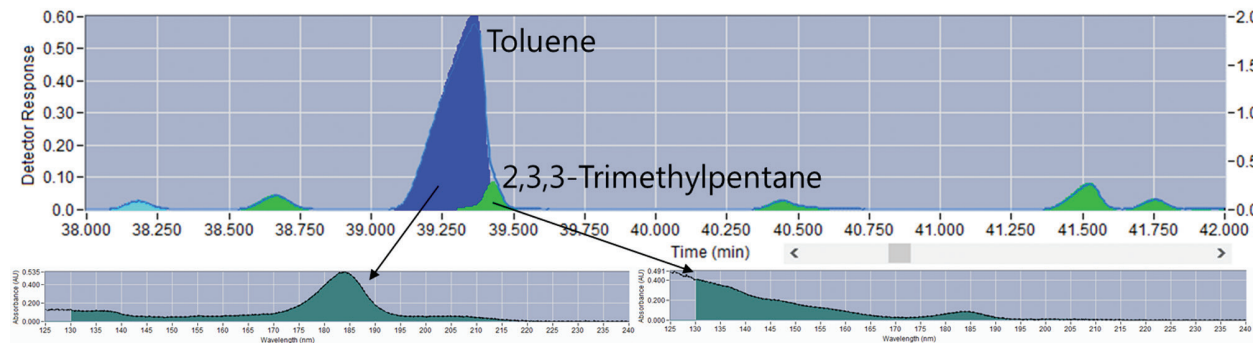


Figure 2: The deconvolution of toluene and 2,3,3-trimethylpentane by VUV PIONA+™. VUV Analyze™ fits spectral profiles with VUV library spectra to provide the identities and/or class and relative concentrations of co-eluting compounds.

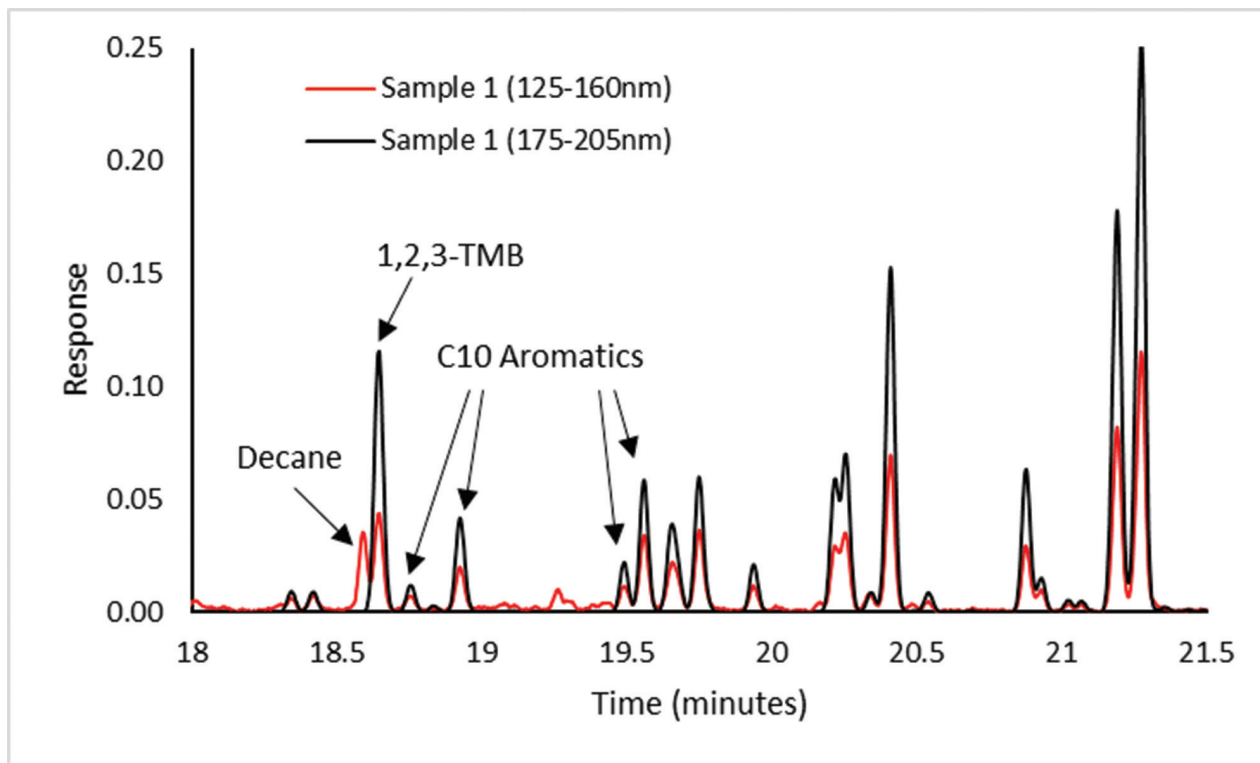


Figure 3: GC-VUV chromatogram of blended gasoline sample containing high aromatic content and low saturate content in the C10-C12 range (~C10 aromatics region shown). Spectral filters have been applied during post-run data analysis to highlight the relative amounts of aromatics (175-205nm, 125-160nm) and saturates (125-160nm) present in the sample. The chromatogram shows the ideal DHA scenario where aromatics peaks can be reliably integrated without interference from co-eluting saturated hydrocarbons.

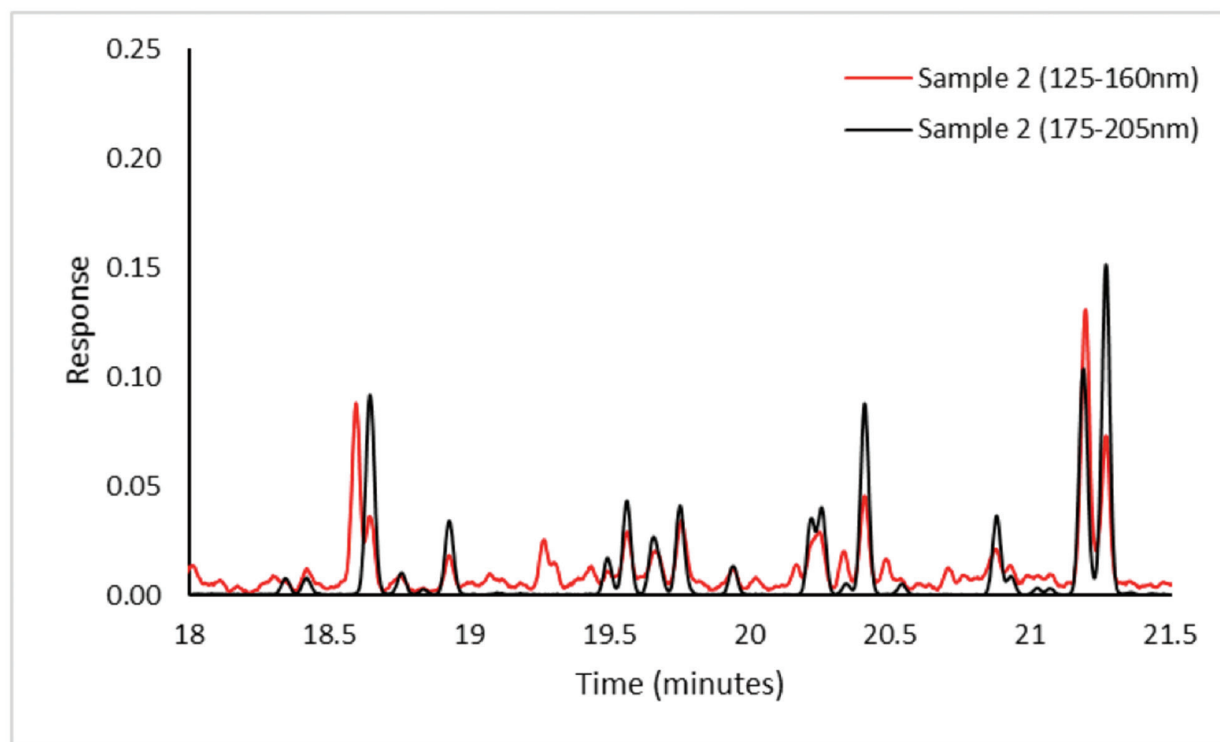


Figure 4: GC-VUV chromatogram of blended gasoline sample containing significant co-elution of saturated hydrocarbons with C10-C12 aromatics (~C10 aromatics region shown). Spectral filters have been applied during post-run data analysis to highlight the relative amounts of aromatics (175-205nm, 125-160nm) and saturates (125-160nm) present in the sample. The comparison shows significant saturate response between and overlapping with the aromatic peaks. VUV PIONA+™ eliminates the error of over-reporting aromatics and under-reporting saturates by using their spectral responses to provide accurate compound class identification and quantitation.

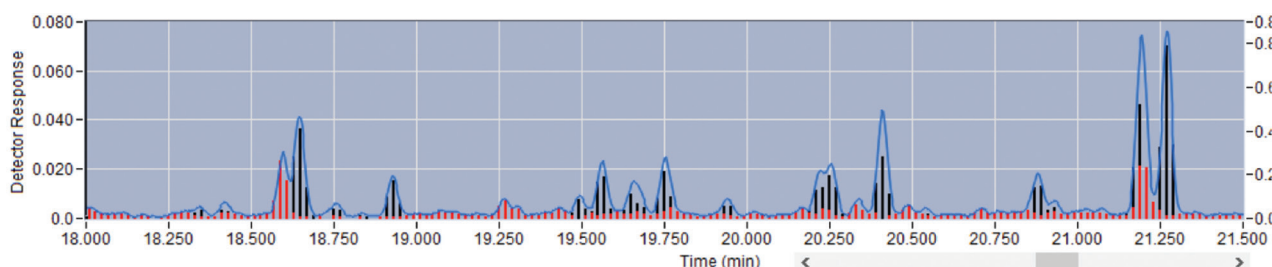


Figure 5: Deconvolved GC-VUV analysis of the blended gasoline sample containing high C10-C12 saturated hydrocarbon and aromatic content. VUV Analyze™ performs time interval deconvolution (TID) to resolve the co-elution of saturates and aromatics in the chromatogram.