

Differentiation and Determination of Fatty Acid Methyl Esters by Gas Chromatography – Vacuum Ultraviolet Spectroscopy

Introduction

Gas Chromatography is a mature analytical technique used predominately for separating and quantifying the components of complex organic chemical mixtures. The addition of mass selective detectors has extended the use (GC/MS) to include compound identification. A wide range of columns and sample introduction techniques allow GC to solve most analytical problems for volatile and semi-volatile compounds. Absorption spectroscopy, although widely used in liquid chromatography has not been widely adopted in gas chromatography due to the relative lack of absorption for most analytes in gas phase within traditional regions of the electromagnetic spectrum. Recent scientific advances have allowed the use of very short wavelengths (120nm – 240nm) where compounds, including those in the gas phase, exhibit strong, characteristic absorption spectra.

In this bulletin we demonstrate the use of a GC detector based on this short wavelength region, known as the vacuum ultraviolet (VUV) region, to identify and quantify a test mixture of 37 saturated and unsaturated fatty acid methyl esters (FAMES). These compounds, originated from animal and vegetable oils and fats, commonly present in biodiesel and various consumer products, provide serious identification challenges for modern mass selective detectors due to the prevalence of isomeric analyte species.

The VUV detector and associated data system acquire full spectral range data at up to 100 Hz sampling rate. Spectral filters can additionally be applied post-run to enhance specificity for compounds of interest. Since compounds of similar structure typically exhibit similar spectral features, the extracted wavelength chromatograms (i.e. the result of applying spectral filters) can be used to selectively analyze specific groups of compounds – in this case the unsaturated versus saturated fatty acids.

Experimental

Due to the limited volatility of fatty acids, a mixture of the esterified versions of these compounds, fatty acid methyl esters (FAMES) were analyzed. Gas chromatographic analysis was completed with the following setup:

Detector: VUV Analytics VGA-100

Gas Chromatograph: Shimadzu model GC-2010

Column: 60m x 0.25mm x 0.25 μ m – SLB-IL111

Text Mix: 37 component FAME Mix – 20 unsaturates (9 mono + 11 poly), 17 saturates – Supelco CRM47885

Results and Discussion

The absorption spectra of the saturated fatty acids show virtually no absorbance at wavelengths longer than 180 nm (Figure 1).

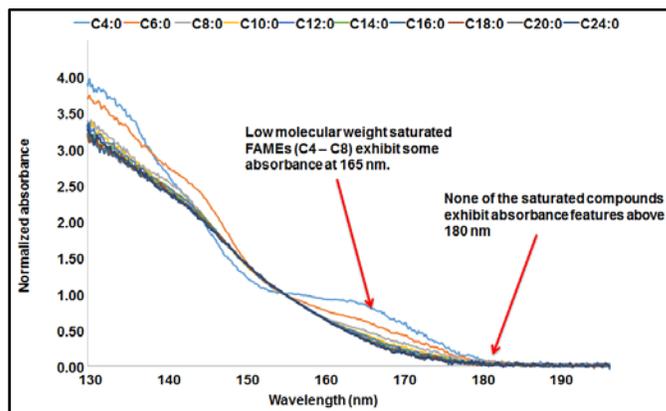


Figure 1. VUV spectra of saturated FAMES

By contrast, the unsaturated fatty acids show strong absorbance features above 180 nm (Figure 2). Absorption in the 170 -200 nm range increases with the number of double bonds allowing to predict the number of double

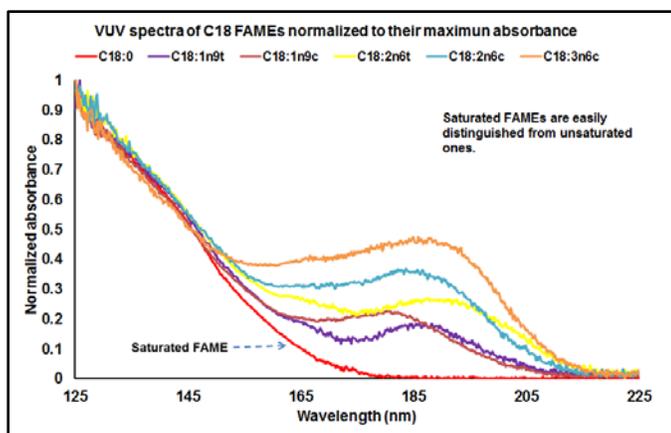


Figure 2. A comparison of the VUV spectra for C18 FAMES

bonds for an unknown fatty acid. VUV technology allows to distinct *cis* from *trans* isomeric mono and poly unsaturated FAMES. The difference in spectral response between the saturated and unsaturated compounds allows the use of spectral filters to “extract” the

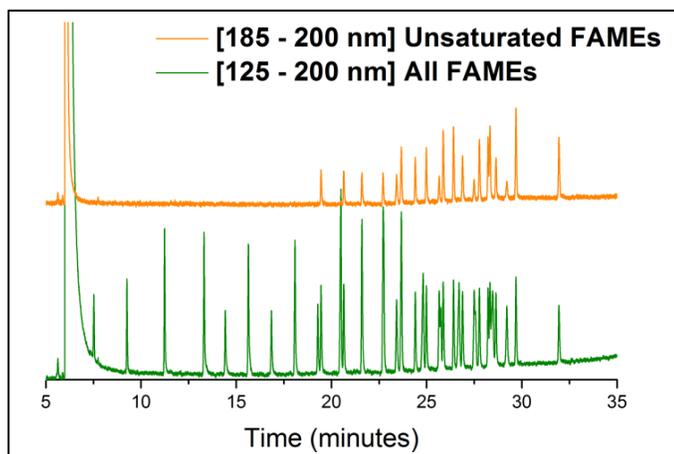


Figure 3. The selectivity of VUV to spectroscopically distinguish the unsaturated FAMES (blue) FAMES

unsaturates from the mix (Figure 3). This use of spectral filters and the resulting extracted absorbance chromatogram allow precise quantitation without the need for complete chromatographic separation of all compounds. Co-eluting saturates and unsaturates were successfully deconvolved.

In addition to the quantitative capability, the technique provides powerful qualitative capabilities as well. Since compounds exhibit a unique spectral response within these VUV wavelengths, comparing the spectra of known pure compounds (in available VUV libraries) with the spectral response of the analyte allows identification of unknowns in the vast majority of cases. Spectra generated on the VGA-100 compare well with spectra generated at synchrotron facilities around the world, giving confidence in the optical precision. Classification of the FAMES as saturates, mono-unsaturates or poly-unsaturates was successful in 100% of cases. A fitting algorithm in the VGA-100 software platform automates these processes.

Conclusion

A new, commercially available VUV detector was applied to the separation and analysis of a FAME mixture. The detector’s ability to distinguish saturates from unsaturates based on wavelength dependent spectral absorbance (in addition to time), provides an additional tool for the chromatographer. VUV spectral matching also provided the capacity for straightforward compound identification and/or classification.



VUV Analytics

715 Discovery Blvd. Suite 502

Cedar Park, TX 78613

Phone (512) 333-0860

www.vuvanalytics.com