Deconvolution of Co-eluting Chromatographic Signals through Vacuum Ultraviolet Spectroscopy

Application Note

Introduction

Gas Chromatography (GC) is a mature analytical technology used predominately for separating and quantifying the components of complex organic chemical mixtures. The addition of mass selective detectors has extended the use of GC 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 the gas phase within traditional regions of the electromagnetic spectrum.

Recent scientific advances[1] have allowed for the use of very short wavelengths (120nm – 240nm), a region where essentially all chemical compounds absorb. The use of this region, which has traditionally been restricted to bright source synchrotron facilities, has been enabled by the use of specially coated reflective optics paired with a back-thinned charged coupled device (CCD) which can simultaneously assess absorption features across the spectrum for peaks eluting from a GC column. The unique, characteristic spectra that result allow for the identification or classification of unknowns as well as the ability to deconvolve co-eluting species including isomeric compounds. The VGA-100 vacuum ultraviolet (VUV) detector is the very first bench-top spectrometer capable of detection in this short-wavelength, VUV region, and can be connected to any standard GC through a heated transfer line. A schematic of the VGA-100, which is capable of capturing full spectra at a sampling rate as high as 100 Hz, is shown in Figure 1.

In this paper we highlight in particular the VGA-100's unique capacity for the deconvolution of co-eluting species. Presented first is an overview of the VUV absorbance fitting algorithm which makes deconvolution possible. Following this, VUV spectral deconvolution is demonstrated in several example applications where chromatographic co-elution is frequently encountered. These applications include the separation of aromatic xylene isomers, long-chain fatty acid methyl ester (FAME) compounds, and permanent gases. In each of these cases, VUV spectral deconvolution eliminates the need for complete chromatographic separation, enabling more efficient analyses.

Experimental

➢ Instrumentation and Standards

A Shimadzu GC-2010 gas chromatograph coupled with a VUV Analytics VGA-100 VUV gas detector was used for all analyses. Various columns were utilized, including an HP PLOT/Q (30 m x 0.32 mm x 20 µm) from Agilent Technologies and an SLB-IL111 capillary column (60 m x 0.25 mm x 0.2 µm) from Supelco. Helium was used as the carrier gas throughout, while argon was used as make-up gas in the detector. Liquid sample injections were delivered by an autosampler at volumes of 0.1 – 0.5 µL with split ratios ranging from 5:1 – 250:1. Gas samples of 0.500 mL volume were injected manually. Both isothermal and temperature programming oven conditions were used.

Standards used for analysis were acquired from various sources. *meta*-Xylene and *para*-xylene standards were purchased from EMD Chemicals-Merck KGaA and J.T. Baker, respectively. A mixture of ten FAMEs in a rapeseed oil standard mixture was acquired from Restek (AOCS #3). Permanent gas samples were collected from the off-gassing of thermally decomposing lithium-nickel-manganese-cobalt-oxide (NMC) batteries.

➢ Absorbance Fitting Algorithm

The model absorbance spectrum where n analytes are simultaneously present in the flow cell is:

[1] Acknowledgments: Hui Fan, Ling Bai & Kevin Schug Department of Chemistry & Biochemistry, The University of Texas at Arlington

VUV ANALYTICS

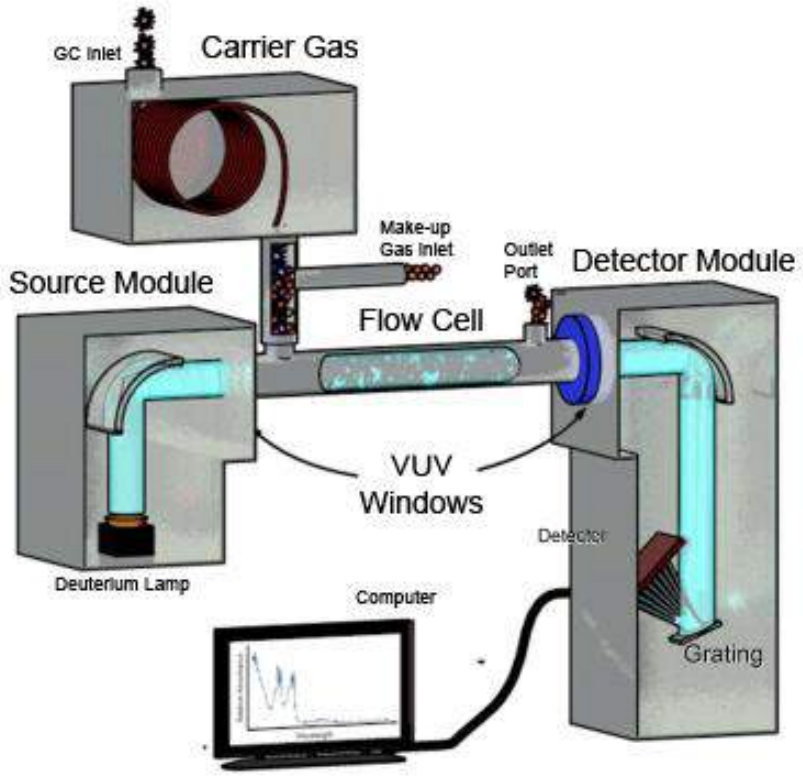

Figure 1. Schematic (not to scale) of the GC-VUV instrument. Dimensions are 13 in. (w) x 30 in. (d) x 17 in. (h). Flow cell volume is ~80 µL. Path length is 10 cm.

Equation 1

$$A_j = \frac{1}{\ln(10)}\frac{d}{V}\sum_{i=1}^{n}\sigma_{ij}N_i = \frac{1}{\ln(10)}\frac{d}{V}\left(\sigma_{1j}N_1 + \sigma_{2j}N_2 + \ldots + \sigma_{nj}N_n\right)$$

where d is the flow cell length and V is the flow cell volume. There is one equation like this at each wavelength value j. Dropping the subscript j to generalize the wavelength dependence:

Equation 2

$$A = \frac{1}{\ln(10)}\frac{d}{V}\left(\sigma_1 N_1 + \sigma_2 N_2 + \ldots + \sigma_n N_n\right)$$

where A is the calculated absorbance spectrum, to be compared with A_{meas}, the measured absorbance spectrum. The σ_i are the cross section spectra (in cm^2/molecule) for each of the components - these cross section tables are normally stored in the VUV spectral library. So for each analyte, there is one term consisting of the product of the number of analyte molecules, N_i and the table of cross section values σ_i. The N_i are the parameters to be optimized, and the factors $1/\ln(10)\, d/V\, \sigma_i$ are the basis functions to be used in the linear optimization procedure (*i.e.*, the fit procedure).

Alternately, the model can be built up from the analyte reference spectra:

Equation 3

$$A = \sum_{i=1}^{n} f_i A_{i,ref} = \left(f_1 A_{1,ref} + f_2 A_{2,ref} + \ldots + f_n A_{n,ref}\right)$$

Here, the f_i are the parameters to be optimized and the $A_{i,ref}$ are the basis functions. The advantage to building the model this way is that the absolute cross sections do not need to be known, although the response will now need to undergo the traditional calibration procedure in order to equate peak areas with analyte amounts. In either case, a set of known basis functions is defined, and a set of scaling factors must be determined by linear optimization.

The result of the fitting procedure is the set of optimal parameters N_i or f_i, depending on whether cross sections or reference spectra were used. These optimal scaling parameters can be put back into Equation 2 or Equation 3, as appropriate, to calculate the fit absorbance spectrum, which ideally differs from the measured spectrum only by the measurement noise.

If analyte reference spectra were used in the model, the optimized f_i are the amount of the i^{th} component relative to the i^{th} reference spectrum represented in the measured absorbance. A more intuitive representation of the results can be obtained by applying one of the integration filters used in the measurement to the reference spectra, to obtain $A_{i,ref,int}$. Then $f_i A_{i,ref,int}$ is the contribution the ith analyte made to the originally measured chromatogram filter. If the model is applied to a region of the chromatogram consisting of many measured data points, a curve representing the contribution of each analyte to the original chromatogram is generated. The areas or heights of these curves can be used to quantify the analyte amounts.

Results and Discussion

➢ Xylene isomers

It is quite common for closely related isomers to have similar or even identical retention times, resulting in co-elution from the column. For example, the *meta*- and *para*- isomers of xylene are particularly difficult to resolve chromatographically due to their similarity in structure. Further complicating their analysis, these isomers are virtually indistinguishable based on electron ionization mass spectral profiles. However, these two compounds can be distinguished based on their VUV spectral response. Co-elution of the xylene isomers is shown in Figure 2, where a single sharp peak with a retention time of approximately 6.30 minutes is seen. Through the use of the aforementioned fitting algorithm, this single

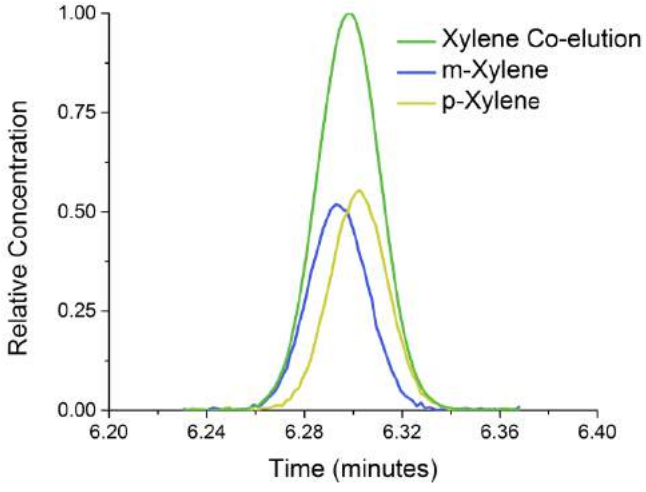

Figure 2. Deconvolution of the overlapping chromatographic signals for m- and p-xylene

(green) peak was successfully deconvolved into additive contributions from both isomers.

➢ Rapeseed oil mixture

A rapeseed oil mixture consisting of ten long-chain fatty acid methyl ester (FAME) compounds was analyzed chromatographically. In this mixture, two compounds, methyl linolenate (C18:3) and methyl behenate (C22:0), displayed nearly identical retention times, as shown in Figure 3. These two species, however, possess distinct VUV absorption spectra on account the difference in saturation between the two compounds (the former is unsaturated while the latter is saturated). More specifically, the absorption profiles of saturated FAME compounds exhibit virtually no absorbance at wavelengths longer than 180 nm, whereas unsaturated FAMEs display strong absorbance features above 180 nm. This clear distinction allowed once again for the deconvolution of these two peaks, as highlighted in Figure 3.

➢ Permanent gases

Gases evolved during thermal runaway events in lithium-nickel-manganese-cobalt-oxide (NMC) batteries were collected and analyzed via GC-VUV. Each battery generated significant quantities of volatile gases, including those that are flammable (e.g., methane, ethylene, and propene) and toxic (e.g., acetaldehyde, 1,3-butadiene, and chloromethane). One instance of co-elution did occur: an oxygen/carbon monoxide peak with a retention time of approximately 3.3 minutes. These two species are key decomposition products in the study of thermal runaway reactions of Li-ion batteries, but unfortunately they are not easily resolved on PLOT/Q columns. Mass Spectrometry (MS) detection is likewise incapable of resolving these co-eluting peaks into their relative contributions. In order to address this issue, alternative column technologies with stronger adsorption mechanisms must normally be employed, which then results in excessive retention of the remaining components.

Successful deconvolution of the oxygen and carbon monoxide chromatographic signals by the VGA-100 is presented in Figure 4. A magnified view of these co-eluted peaks in the NMC chromatogram is shown in Figure 4A. Figure 4B then displays the VUV absorption spectrum observed at the chromatographic peak maximum (labeled: 'Original') as well as the individual VUV spectra for oxygen and carbon monoxide from the VUV spectral

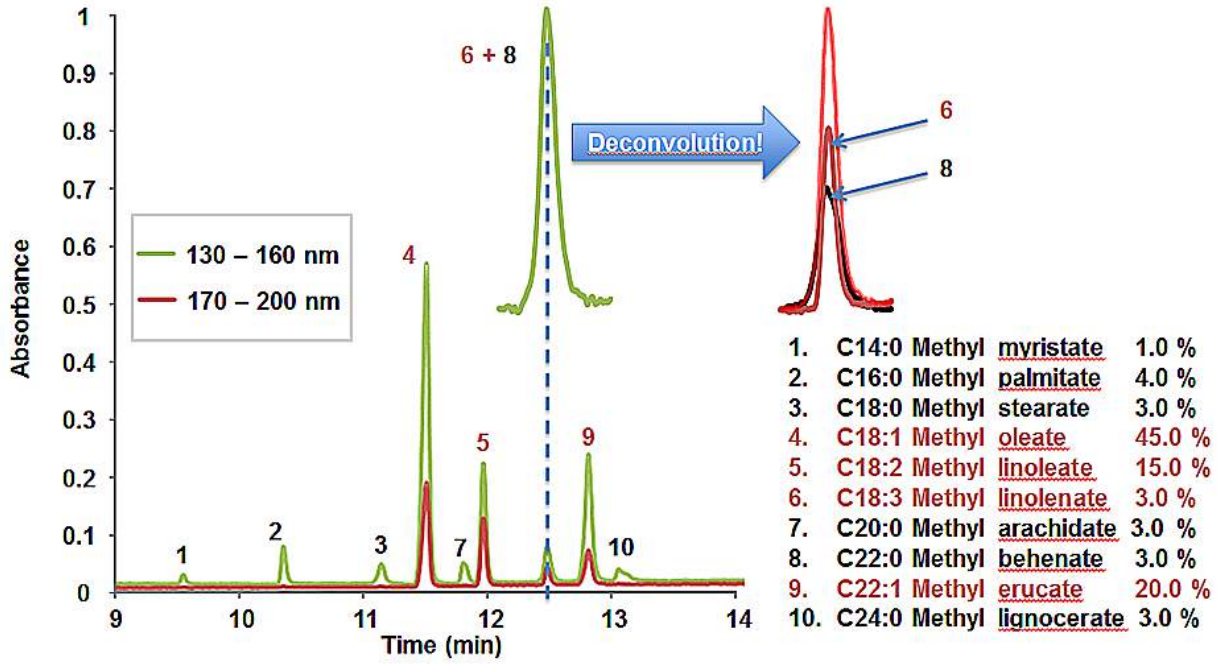

Figure 3. Rapeseed oil mixture chromatogram highlighting the deconvolution of peaks 6 and 8. Unsaturated FAMEs absorb strongly at 170 – 200 nm wavelengths, while saturated FAMEs do not.

library. There is a clear contrast in these two spectra – while the oxygen spectrum consists largely of one broad hump spanning 130-175 nm, the carbon monoxide spectrum possesses numerous sharp vibrational features in this same range. This marked difference in the spectral responses of the two species enables their efficient deconvolution. Thus, the 'Original' spectral response is readily decoupled into relative contributions of oxygen and carbon monoxide, which the algorithm then uses to construct a deconvolved chromatographic response (Figure 4A).

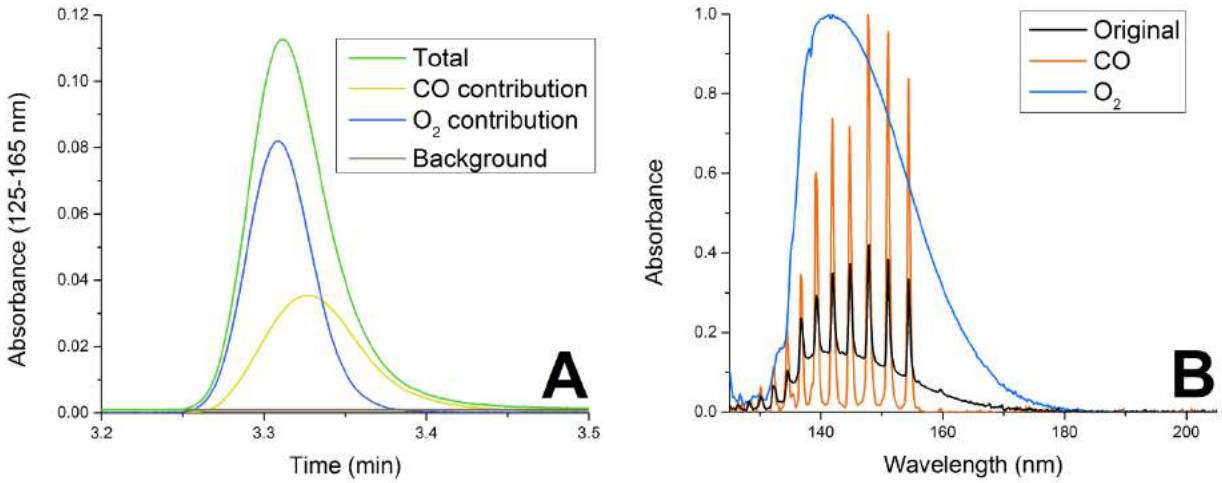

Figure 4. Deconvolution of co-eluting CO and O_2 chromatographic peaks from the off-gassing of the NMC battery sample (A) using the distinct VUV spectral contributions obtained at 3.30 min (B).

Conclusion

GC detection via VUV absorption spectroscopy offers a fundamentally new means of identifying and differentiating peaks. With high resolution VUV spectra, the VGA-100 provides the capacity to distinguish closely related compounds and even deconvolute co-eluting spectrally distinct species. This ability proved absolutely critical in each of the applications highlighted here. MS detection, while powerful, often struggles distinguishing isomeric, isobaric, small, or labile compounds. Thus, VUV detection certainly has the promise to meet or exceed the capabilities of MS, or at the very least will become a powerful complementary and orthogonal detection technique.

VUV Analytics
715 Discovery Blvd. Suite 502
Cedar Park, TX 78613
Phone (512) 333-0860

www.vuvanalytics.com