DEVELOPMENT OF QUALITATIVE AND QUANTITATIVE APPLICATIONS IN ENERGY INDUSTRY USING GAS CHROMATOGRAPHY- VACUUM ULTRAVIOLET SPECTROSCOPY

by

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Abstract

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Characterization and evaluation of hydrocarbon assets, including content of linear and branched alkanes, cycloalkanes, aromatics, olefins, and naphthenes, among others, during production and distribution are very crucial in oil and gas industries. Quantification and qualification of bulk composition of hydrocarbon groups in complex samples like gasoline, diesel, and other high value refinery products is very challenging. Gas chromatography (GC) is the most popular technique among the petrochemical industry and many of the EPA and ASTM methods have been established based on GC for analyzing hydrocarbons in complex mixtures. Though there are many methods available, there are still limitations on the existing methods. Vacuum ultraviolet spectroscopic absorption detection (VUV), a recent and impactful GC detector has been evaluated and investigated in this research on characterization of different components in oil and gas mixtures. The vacuum ultraviolet detector (VUV) is a non-destructive mass sensitive detector for gas chromatography that continuously and rapidly collects full

wavelength range absorption between 120 and 240 nm. Samples ranging from gaseous mixtures, such as natural gas and lithium ion thermal runaway out-gassing to fossil fuel samples, including gasoline and diesel fuels, were analyzed to demonstrate the potential power of VUV coupled with GC. GC-VUV was shown to be a worthy alternative tool to other existing techniques on complex mixture quantitative and qualitative analysis, especially in terms of its complementarity to mass spectrometric detection.

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Chapter 1

Introduction to dissertation

1.1 The significance of fossil fuel and fossil fuel analysis

Fossil fuels, as very important energy resources, have very significant impact and importance to the market and the society. Fossil fuels are concentrated organic compounds created from the remains of plants and animals, which lived millions of years ago and were deposited in the earth's crust. They can be extracted from either underground or undersea deposits. These resources help humans to generate stream, electricity, and provide a key component to the transportation system. Fossil fuels make modern life possible. Nearly 80% of the US energy demands are met using fossil fuels, it enables economic growth to happen [1].

Fuels can be classified into two classes, fossil fuels and alternatives to fossil fuels [2]. The most common products derived from fossil fuels are gasoline used for automobiles (45.3%), diesel fuels and heating oil (29.8%), other synthetic chemical derivatives from fuel (19.4%), jet fuel (9.7%), and asphalt (2.1%) [2]. The use of these fuel products makes modern transportation possible; people and goods can be moved around the world and fuels make manufacturing of millions of goods possible. An estimation has been made by the energy information system administration that the usage of fossil fuels will remain very high till 2040, supplying 80% of US's energy needs [3]. The exploration of the oil reserves has also been continuously performed with new technologies and discoveries which maintains the high consumption of fossil fuels [4]. Because of the huge significance and usage of fossil fuels, characterization of hydrocarbon components contained therein, like linear and branched alkanes, cycloalkanes, aromatics, olefins, and naphthenes, among other groups of compounds in

different fossil fuel products is crucial. Oil and gas industries and environmental agencies have been continuously developing advanced methods to analyze hydrocarbons products in complex oil and gas samples, to be used during exploration, production, and distribution.

1.2 Gas chromatography as a tool for fossil fuel analysis.

Chromatography is a separation method where the components are separated based on the partitioning process between the components and the stationary phase. Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for analysis of volatile and semi-volatile compounds that has been discovered since 1952 [5]. It is a very mature and popular technique that the worldwide market of GC instruments is estimated to be up to nearly $1 billion annually [6]. In GC, the sample is vaporized and carried through the stationary phase by the mobile phase gas. Usually an inter gas is used such as helium, nitrogen, and hydrogen. Analytes in the sample are separated based on their relative boiling points and affinities for the stationary phase [6]. Gas chromatography is one of the most premier techniques used in the fossil fuel analysis among oil and gas industries.

GC columns play an important role in GC separation as the stationary phase is the heart of separation. Packed columns and capillary columns are the two most common column types. Packed columns are packed with fine, inert particles and normally are 1.5-10 m in length and have an internal diameter of 2-4 mm [7]. They provide for very good sample capacity and low cost, but they have poor efficiency. Capillary columns, also known as open tubular column, have a stationary phase coated on the inner surface of

the capillary wall. They provide much better efficiency (narrow peaks) which leads to greatly improved peak separation [8, 9].

There are two common types of open tubular columns including porous-layer open tubular (PLOT) column and wall coated open tubular column (WCOT) [7]. The inner diameter of an open tubular column is between 0.25 and 0.5 mm and can be up to 100 meters long [10]. Figure 1-1 shows the different types of column including packed capillary column, porous layer open tubular column, and wall coated open tubular column (WCOT).

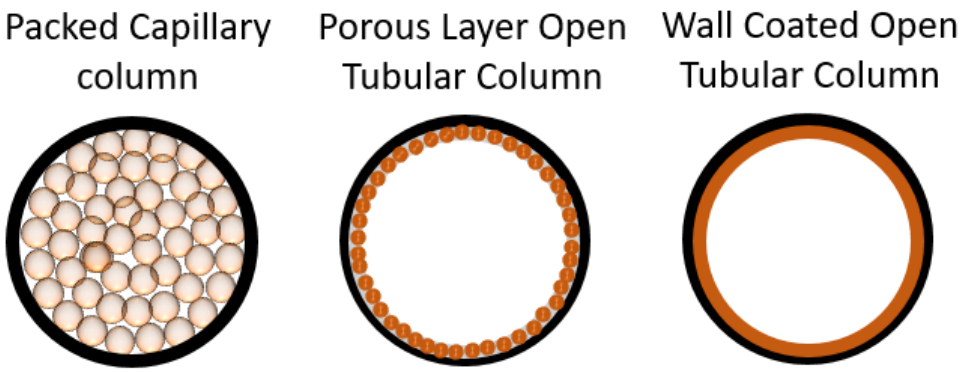

Figure 1-1 Gas Chromatography Columns

Wall coated column is the most popular open tubular column consisting of a fused silica capillary tube with its inner wall surface coated with a thin layer of liquid stationary phase. Porous-layer open tubular columns have a solid layer of materials coating the inner wall of the column. It has high inner wall surface that holds stationary phase with film thickness between 5 and 50 micrometers that is mainly used as adsorption or

molecular sieve of low molecular weight gases and hydrocarbons such as hydrogen, helium, nitrogen, oxygen, methane, ethane, and other light gases [7][11].

The use of GC requires its combination with an appropriate detector to provide desired qualitative and quantitative information. The flame ionization detector (FID), thermal conductivity detector (TCD), electron capture detector (ECD), and mass spectrometer detector (MSD) are most common detectors that are used for oil and gas analysis. FID is one of the most frequently used detectors for GC analysis. Its operation is based on the detection of formylium ions (CHO^+) formed during the combustion process in a hydrogen flame. The generation of the formylium ions are proportional to the concentration of carbon containing compounds in the sample. It can be used to detect organic/hydrocarbon containing compounds with very low detection limits [12]. TCD, another common GC detector, measures the changes in the thermal conductivity when an analyte is present, and compares it to a reference flow with helium or nitrogen, which serve as the carrier gas. The reduction of the thermal conductivity is measured as the signal when the analytes elute to the detector [10]. It is a non-specific universal detector with relative low sensitivity compare to other detectors. ECD is used for detecting high electronegativity components, it detects analytes in a gas stream through the attachment of electrons via electron capture ionization. The ECD can have much more sensitivity than the FID and TCD for the analysis of halogenated compounds [10]. MS is a very powerful instrument that measures the analytes based on the mass-to-charge ratio with very high efficiency and sensitivity. It can be applied in a wide range of analysis [10].

Two-dimensional GC has been introduced for very complex mixture analysis, and it has been largely applied in oil and gas industries. The schematic of 2D GC is showing in

Figure 1-2. As it is shown is the figure, samples are normally injected to the first GC Column at the head of the 1D column, after the analytes eluted from the 1D column, they will undergo the process of the modulator and then diverted to the second column where analytes can go through a further separation. Eventually, they will reach the detector located at the end of the second column [13]. The columns used for 2D GC must be different in both dimensions and nature of the stationary phase to obtain better separation and excellent resolution. Basically, the columns are orthogonal, the first column, is typically a non-polar column about 20-30m, the second column, normally a polar column is typically shorter to provide faster separation. [14]. 2D GC provides very powerful separation and comprehensive results with very complex sample constituents like gasoline and diesel [15, 16].

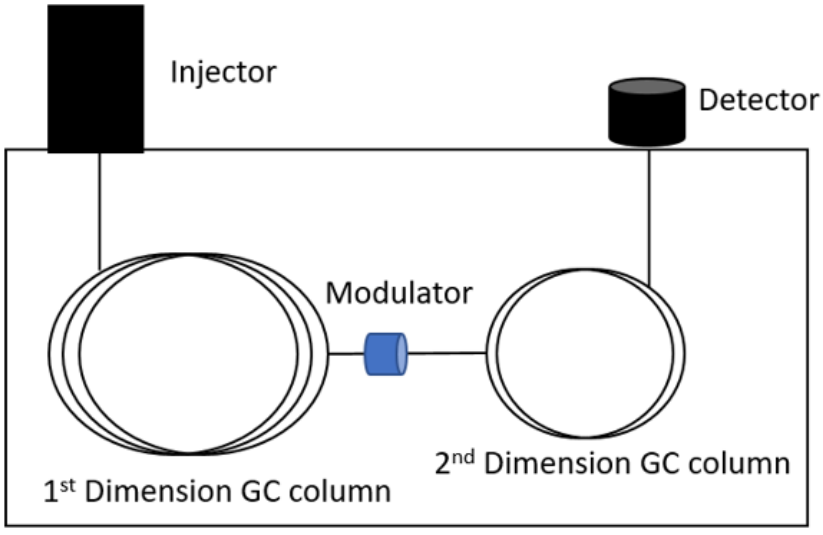

Figure 1-2 Two-dimensional Gas Chromatography

1.3 Application of gas chromatography for natural gas

Permanent gases, including hydrogen, helium, oxygen, nitrogen, argon, carbon monoxide, and carbon dioxide, are very important resources among chemical and energy industries [17]. Analyzing permanent gases with a very efficient and accurate method is very challenging. Natural gas consists of methane, ethane, propane, carbon dioxide, oxygen, nitrogen, hydrogen sulfide, and other rare gases, and is a very important fossil fuel that is used for many different purposes [18]. It is the cleanest burning petroleum-based fuel and can be used for heating, cooking, and electrical power generation. In the US, about 29% of the energy is provided by natural gas; it is used to heat half of the homes in the country. It is the fastest growing primary energy source in the world due to its higher energy efficiency and reduced greenhouse emissions, relative to other fossil fuel products [19, 20].

The consumption of and exploration for natural gas reserves have been continuously rising in the past decades, and it is predicted to keep increasing for the next 15 years [19]. However, methods used for natural gas extraction, such as hydraulic fracturing, have given rise to unanswered questions regarding to some environmental impacts. Concerns about ground water contamination and other environmental problems generated from natural gas extraction based on hydraulic fracturing techniques have increased dramatically [21].

Methane can be dissolved in a gaseous state in confined aquifers with very high concentrations – much greater than the saturation concentration at atmospheric pressure. Within 28 mg/L of methane in water, methane becomes saturated, and when it reaches 5% by volume, it becomes flammable [22]. When water with high concentration

of natural gas is exposed to atmospheric pressure, the natural gas will be released. Depending on the concentration, this can be a hazard with respect to flammability or asphyxiation to humans and animals if released in confined spaces. High methane concentrations have been detected in many different groundwater resources, which is considered hazardous [23]. In addition, permanent gases like methane, nitrous oxide, and carbon dioxide are some of the main contributors to climate change. Therefore, influences from natural gas leakage to the environmental has become a major issue, and identifying the origin of water contamination has become very important [24, 25].

There are challenges with characterizing and accurately quantifying permanent gases from various sample types. None of detectors introduced above are perfect for the analysis of highly volatile compounds, like permanent gases. FID has good sensitivity and a wide linear range but it only detects carbon containing compounds and it is a non-specific detector. ECD only detects compounds that have very high electron affinity, for instance halogenated compounds. TCD is a universal detector but it is also non-specific and has low sensitivity. MS has very excellent sensitivity and great capability for analyte identification; however, it becomes limited when applied to very small molecules (higher noise) and isomers (identical molecular weight) [26].

Many American Society for Testing and Materials(ASTM) methods have been developed to analysis natural gas. ASTM D1945 was developed for analysis of natural gas by gas chromatography [27]. ASTM D2163 is the standard test method for determination of hydrocarbons in liquefied petroleum gases and propane/propene mixtures by gas chromatography [28]. Both methods require multiple detectors including ionization discharge detector (BID), FID, and TCD. Both methods require sampling loop with back flush of pre-column to vent for elution of different set of analytes [29]. Thus,

developing a new method for permanent gas analysis with a straightforward method with high separation power is very necessary. In order to develop a method that can detect all these small molecules and permanent gas species at the same time with better resolution, a new detector vacuum ultraviolet spectroscopy (VUV), which is introduced in Chapter 2, coupled with GC has been applied and evaluated to achieve this goal. The details about the application is introduced in Chapter 3.

1.4 Application of gas chromatography for gasoline and diesel analysis

Gasoline and diesel fuels are the most important resources derived from fossil fuels. As it has been introduced above, the consumption of gasoline and diesel fuel is very high and nearly 45% and 30% of crude oil are refined to gasoline and diesel fuel, respectively. Gasoline naturally contains over 500 hydrocarbons from C3-C12 that can be classified into different groups including paraffins, isoparaffins, aromatics, naphthenes, and olefins [30, 31]. Diesel fuel has very high power-efficiency and economical features that makes the demands and consumption very high. It contains very complex chemical components ranging approximately from C10 to C22 and including many different isomeric species. As the hydrocarbon chain gets longer, more complex structures isomers appear, which makes the identification more difficult. Thus, due to the complexity of gasoline and diesel fuel, the characterization and quantification are very challenging.

Initially, one-dimensional gas chromatography is mostly applied for gasoline and diesel fuel analysis coupled with detectors like flame ionization (FID) and mass spectrometry (MS). High-performance liquid, supercritical fluid chromatography, infrared, ultraviolet, fluorescence, and nuclear magnetic resonance spectroscopy have all been

used for fuel analysis. However, due to the extreme complexity of gasoline and diesel fuel, comprehensive data are very difficult to obtain from these techniques [32]. Different methods applying different techniques have been developed to assist gasoline and diesel fuel analysis. For example, the Unites States Environmental Protection Agency (EPA) methods 8020 and 8021 can be used to analyze fuel samples that utilize the photoionization detector (PID) to determine the halogenates and various aromatic volatile organic compounds [33, 34]. EPA method 8015 applies a flame ionization detector (FID) to determine the various nonhalogenated volatile organic compounds and semivolatile organic compounds [35]. In addition, oxygenates are the most important fuel additives in gasoline contain C1 to C4 alcohols and ethers that help fuel to combust more completely due to the presence of oxygen [36-38]. There are challenges on analyzing oxygenates in gasoline too. American Society for Testing method D4815 was published for determination of C1 to C4 alcohols and MTBE in gasoline by gas chromatography with two dimensional columns and TCD and FID detector [39]. Diesel fuel has more complexity than gasoline and there are very limited test methods for diesel fuel analysis. ASTM D5186 is a standard test method for aromatic determination. Aromatics in the diesel sample are separated and detected using FID detector [40]. These methods are all very useful on different gasoline and diesel fuel applications but with disadvantages and limitations. PID is only sensitive to double bonds and halogenated compounds. FID is sensitive but it is a non-selective detector and it cannot handle the interference from many for other non-targeted compounds in very complex samples. MS provides great results on unidentified compounds but it cannot resolve coeluting species. They are limited to a certain group of compounds, none of them can provide a comprehensive separation of gasoline and diesel fuel components. In addition, most of them requires sampling loop with back-flushing system which makes the methods complicated.

Multidimensional GC coupled to MS has then been developed to determine the components in gasoline and diesel fuel simultaneously and provides very excellent separation [41]. Though it has much more advantage over one dimensional GC, and has certainly grown in popularity, it still has limitations. It is not user-friendly and relatively harder to operate and maintain because of additional hardware and software requirements. In addition, developing and optimizing modulator, the modulator time, and the avoidance of wrap around is very challenging. The costs of equipment and maintenance are also expensive. Therefore, even GCxGC has striking benefits that enables the separation of over hundreds of compounds with its excellent resolution and sensitivity, further developments are needed with respect to instrument operation and data analysis [42].

Diesel fuel spills are one of the main concerns among the environmental society. Due to its toxicity, diesel spills can cause many problems. They threaten natural marine resources, wildlife, and habitats when they occur. It can contaminate soils and ground water and cause damages to microorganisms and plants if it spills into ground [43-45]. Thus, among the environmental forensics society, identifying and characterizing diesel spills and linking the spills to the original suspected sources is a very important and challenging task.

The composition of diesel that is released to the environment will be changed due to different biochemical and chemical process. Hydrocarbons are subjected to these weathering processes including evaporation, emulsification, dispersion, biodegradation, and photooxidation [46, 47]. Diesel fuel contains more than 2000 hydrocarbons and the changes in concentration ratios of some of these compounds are very useful as indicators for diesel oil weathering assessment. Biomarkers are also very useful

indicators in fuel analysis for oil and gas characterization and age identification. n-Alkanes, like C17 and C18, are the highest abundance compounds in fresh diesel, and isoprenoids are the most predominant biomarkers in weathered and biodegraded diesel. Differences in their ratios due to weathering process are very useful for identification of the age of oil and oil spills [46, 47]. Pristane and phytane are showing in figure1-3, they are the two important isoprenoids that serve as biomarker indicators in diesel fuels because of their large abundance and relative ease of measurement [47].

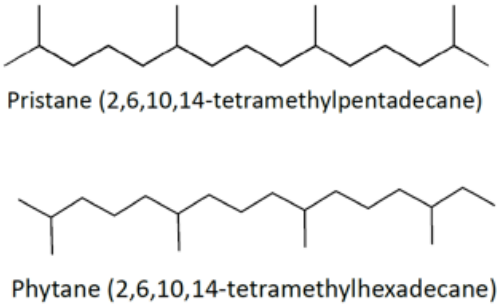

Figure 1-3 Biomarker structures of Pristane and Phytane.

However, the presence of the biomarkers is still relatively very low compare to other major components which makes them difficult to detect and errors are very easy to be introduced when one is integrating them due the interference from other compounds in a very complex mixture [46].

Fingerprinting is one of the most important technique that has been applied for a long period of time where different class of compounds can be compared to identify the source of spilling and age identification measurements [48, 49]. Diesel fuel contains several different classes of compounds including alkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes, and anthracene/phenanthrenes that can be used for fingerprinting. It is a very challenging and complicated task to do diesel fuel fingerprinting. Due to the

weathering process, the composition of diesel fuel will be largely changed. This makes it even difficult to locate the useful compounds that can be used for fingerprinting [32].

Fingerprinting chemical data is very important and must provide sufficient data to characterize the specific types of petroleum component present at a site. Accurate diagnostic informant is very important to allocate the relation between the suspected sources and oil spills and further identify the age of the spills [50]. Vacuum ultraviolet spectroscopy coupled with GC has been applied and evaluated to compare the performance with 2D GC. Results showed that GC-VUV is a good alternative tool to 2D GC on complex mixture analysis for forensic chemist with more straight forward means. Details in methods and results are given in Chapter 4.

1.5 Quantification methods development for complex mixtures analysis.

Not only qualitative analysis of complex mixture is challenging, quantitative analysis of complex mixtures like fuel products is also very challenging. Quantitative analysis is always an essential and fundamental branch of chemistry that assist chemists to determine the concentration of the compounds of interest [10, 51]. Calibration process are always involved in quantification analysis which can largely eliminates the interference from the various systematic errors [52]. However, calibration process involved quantification are always time consuming and costly. It will be much more difficult and time consuming when quantification of complex mixture is required.

A research of developing new calibrationless quantitative analysis based on gas chromatography - vacuum ultraviolet spectroscopy detector has been introduced in this research. Gas chromatography-vacuum ultraviolet spectroscopy has the ability to

quantify and identify analytes based on known absorption cross-sections of gas phase molecules in the VUV regime without calibration. Formula 1 shows the equation of the well-known Beer-Lambert Law.

$$A(\lambda) = \frac{1}{\ln(10)} \sigma(\lambda) \frac{N}{V} d \qquad (1)$$

where σ is absorption cross section (cm^2/molecule), and is similar to wavelength-dependent absorptivity coefficient. N is the number of analyte molecules, V is the sample cell volume, and d is the light-path length. This formula can be derived to the following formula 2 to find the total number of on-column molecules and then to be used to determine the on-column mass directly by GC-VUV.

$$PA = \frac{1}{\ln(10)} R \frac{d}{F} \Sigma N_{col} \qquad (2)$$

where Σ is the absorption cross section integrated over the same wavelength region, R is the detector scan rate, N_{col} is the total number of analyte molecules introduced on column and F is the sample cell flow rate. Thus, as long as the peak area (PA) can be determined and the rest of the instrumental parameters are available. The on-column mass of the analytes will be simply identified without calibration process involved. Benzene and natural gas sample have been analyzed to evaluate the accuracy of precision of this method. Details in methods and results are given in Chapter 5.

Another calibrationless quantification method is also been developed for complex mixture analysis. Gas chromatography-flame ionization detector has been developed for a long time and has gain very high popularity among GC applications for both qualitative analysis and quantitative analysis [53, 54]. Quantification based on FID analysis are

often time very reliable but when it comes to molecules with heteroatoms and high functional groups, the results become less reliable. The FID does not respond to the molecules that have a large number of heteroatoms equally to other molecules that do not contain heteroatoms [55]. For instance, organic compounds with highly functionalized group and heteroatoms containing oxygen, nitrogen, sulfur, or halogens have relatively lower responses compared to hydrocarbons. A system called Polyarc® system that has been developed has the ability to optimize the quantification results of such molecules by combust all the analytes to methane before reaching the FID. Figure1-4 shows the schematic of the Polyarc® system.

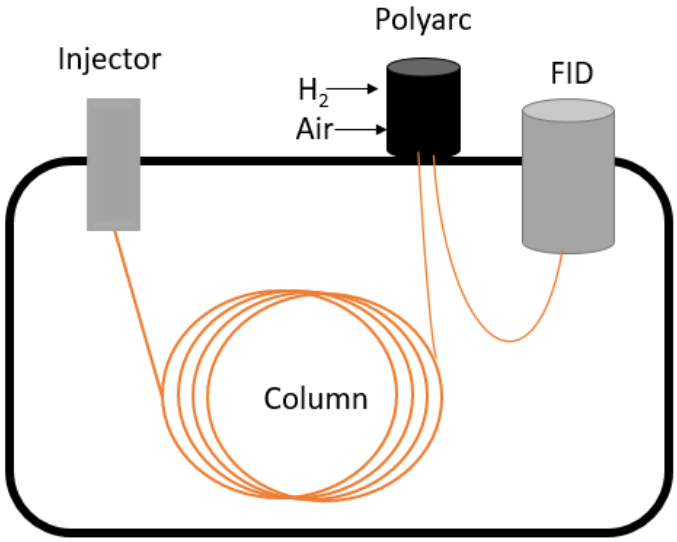

Figure 1-4 Polyarc® system

This system contains two catalytic microreactors that converts all organic compounds to methane before they reach the FID detector. Everything is combusted in the first reaction chamber to CO_2 and reduced in the second reaction chamber to methane before it reaches FID [56]. Because all the compounds are converted to

methane, and due to its universal response, it gives equal response factor for all the organic compounds. And therefore, the carbon content and concentration of an analyte can be determined based on its own response with the facility of another internal standard combined with the formula below:

$$RF = 1 = \frac{mol\ C / area}{mol\ C_{std} / area_{std}} \Longrightarrow mol\ C = \frac{area * mol\ C_{std}}{area_{std}} \quad (3)$$

With this new quantification method, calibration process is no longer needed and only a proper internal standard is needed, which will significantly save time and cost when very complex mixture is analyzed. In this work, different samples ranging from C7-C40 n-alkanes standard, terpene mixtures, polymers mixtures, and gasoline samples have been analyzed on GC-polyarc/FID to fully investigate the its capability on both quantitative and qualitative analysis for complex mixtures. It has proved that the GC-polyarc/FID system has very good quantification ability and accuracy on quantitation analytes in complex mixture samples with reduced cost and labor needed. Details on methods and results are given in Chapter 6 and 7.

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Chapter 2

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

The gas chromatograph has been a mainstay of analytical measurements in the petrochemical industry since the 1950s and 1960s. 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 characterized 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 characterize 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.

Another recent and impactful GC development was the introduction of the vacuum ultraviolet spectroscopic absorption detector (VUV) [1,2]. Prior to 2014, when the detector was commercialized, absorption measurements in the vacuum ultraviolet regime (< 180 nm) were largely relegated to bright source synchrotron facilities. As illustrated in Figure 2-1, through the use of a deuterium lamp, reflective optics, and a charge-coupled device, the benchtop VUV system can 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 analyzed. Concentration-dependent absorption follows the Beer-Lambert Law. Thus, the VUV, like the MS, is a GC detector that has capabilities for both qualitative and quantitative analysis.

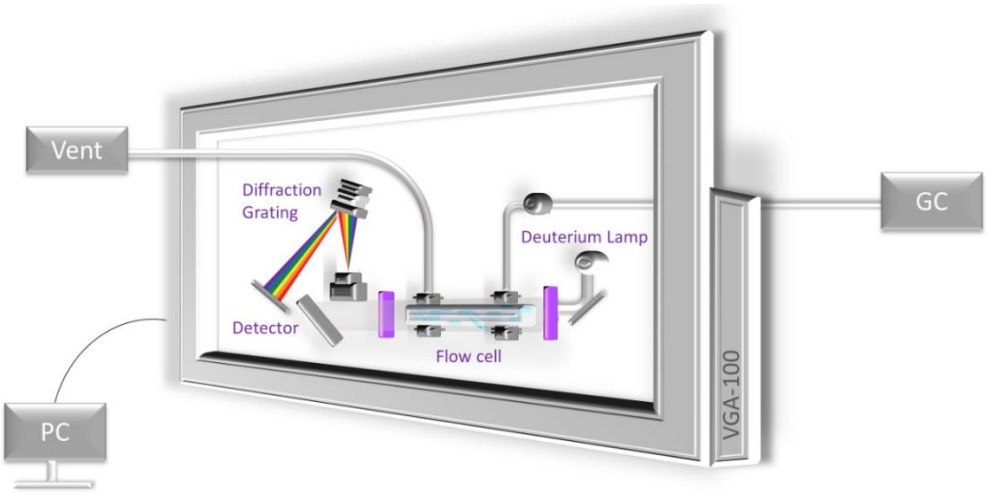

Figure 2-1 Generalized schematic of the VUV detector (VGA-100) from VUV Analytics, Inc.

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 σ → σ* transitions; alkanes absorb fairly strongly in the range of 120 – 160 nm. 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 ionization 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, but this number is also growing rapidly as new adopters contribute additional applications.

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 source and monitor the degree of weathering of diesel fuels introduced into the environment [3]. 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 [4-7]. Nevertheless, for the large range of linear, branched, and cyclic saturated hydrocarbons that occur in petrochemical mixtures, GC separations are still essential for chromatographically resolving homologous series.

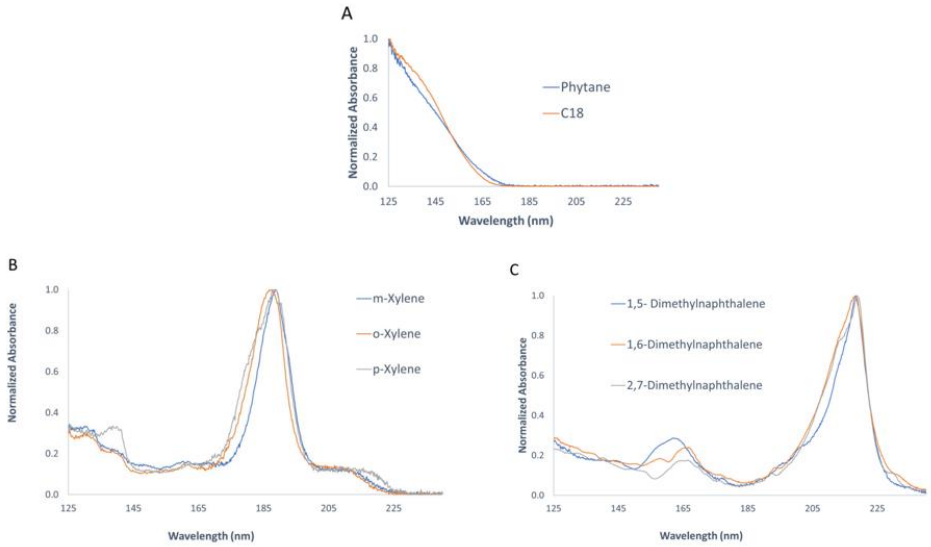

Figure 2-2 Spectral overlays to show spectral differences for A) branched and linear alkanes, B) xylene isomers, and C) dimethylnaphthalene isomers.

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 pg on-column detection limits). Also, as expected, the strong absorption features associated with the π → π* transitions in aromatic compounds are at longer wavelengths (lower energies) compared to the spectral features observed for saturated compounds. Whereas electron ionization mass spectra for each of the xylene and dimethylnapthalene 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 [8].

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 normalized 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.

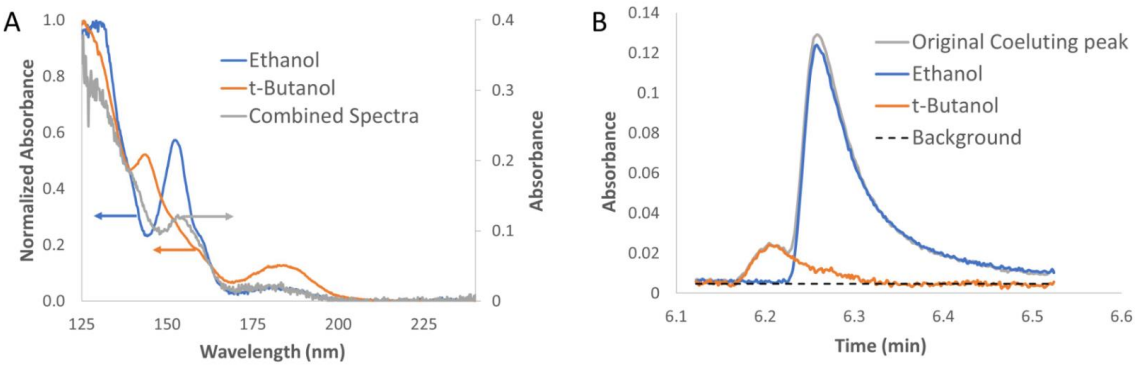

Figure 2-3 Deconvolution of the coelution of gasoline oxygenates: A) shows the combined observed spectrum and the normalized spectra for the individual compounds, while B) shows the combined

observed chromatogram and the deconvolved individual contributions of each compound to the total signal.

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 [4]. It was shown that if one of the isomers was present at reasonable quantity (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 [6], and even deuterium-labeled isotopologues of various analytes [7]. In those cases, spectral similarity 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.

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 characterize 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 characterized 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 [9], and recently an ASTM method (D8071) [10] 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 [11]. Samples that can be well characterized 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.

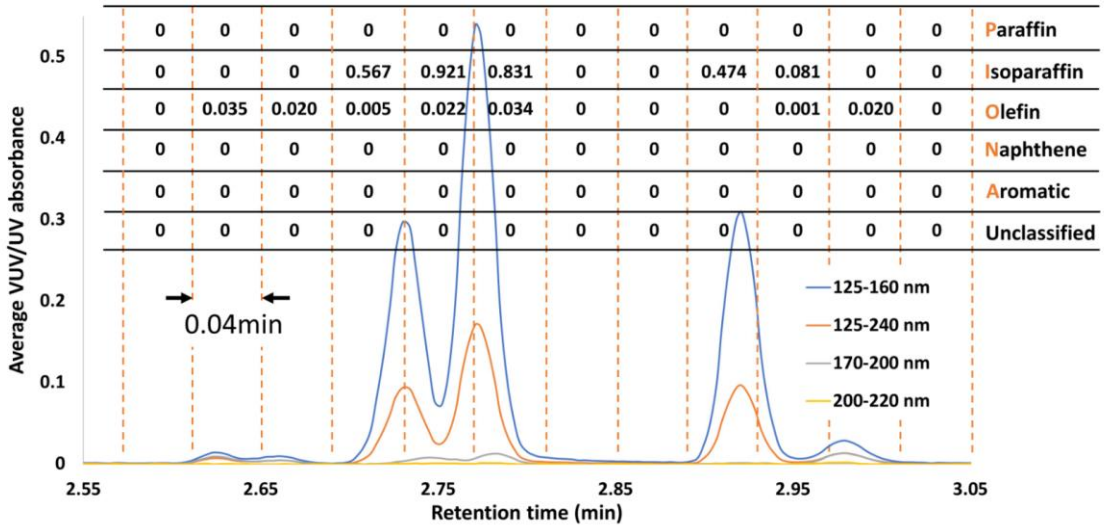

Figure 2-4 A representation of time interval deconvolution. A short portion of a gasoline sample chromatogram is shown divided into time intervals for which the absorption of PIONA class compounds is determined for each interval. This analysis would be perfectly rapidly and in an automated fashion across 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.

Other groups besides ours have shown that the VUV detector is highly applicable for the characterization of different fuels, especially in combination with the aforementioned use of ionic liquid stationary phases [12] and comprehensive multidimensional separations [13, 14]. 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 characterize spectra measured for compounds that may not be available to measure separately and enter into the library. A newer generation detector has been recently introduced, which features a wider absorbance wavelength range (220 – 420 nm), higher operating temperature (420 ^{o}C), and increased sensitivity. This should further expand the application base to higher distillate products, for which much more limited characterization 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 realized; however, its applications in the petrochemical industry has already demonstrated its usefulness and high degree of complementarity to other available detection techniques, especially MS.

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Chapter 3

Permanent gas analysis using gas chromatography with vacuum ultraviolet detection

3.1 Abstract

The analysis of complex mixtures of permanent gases consisting of low molecular weight hydrocarbons, inert gases, and toxic species plays an increasingly important role in today's economy. A new gas chromatography detector based on vacuum ultraviolet (VUV) spectroscopy (GC–VUV), which simultaneously collects full scan (115–240 nm) VUV and UV absorption of eluting analytes, was applied to analyze mixtures of permanent gases. Sample mixtures ranged from off-gassing of decomposing Li-ion and Li-metal batteries to natural gas samples and water samples taken from private wells in close proximity to unconventional natural gas extraction. Gas chromatography separations were performed with a porous layer open tubular column. Components such as C1–C5 linear and branched hydrocarbons, water, oxygen, and nitrogen were separated and detected in natural gas and the headspace of natural gas-contaminated water samples. Of interest for the transport of lithium batteries were the detection of flammable and toxic gases, such as methane, ethylene, chloromethane, dimethyl ether, 1,3-butadiene, CS2, and methyl proprionate, among others. Featured is the capability for deconvolution of co-eluting signals from different analytes.

3.2 Introduction

Permanent gases, those chemical compounds that do not liquefy under ambient conditions, are of great interest in the petrochemical, chemical, and energy industries [1]. Natural gas has emerged as a versatile source of energy in the past decade. As a highly traded international valuable commodity, there is a significant demand for natural gas analysis. Natural gas mainly contains methane, but also ethane, propane, and other minor constituents such as carbon dioxide, hydrogen sulfide, nitrogen, and longer hydrocarbons, ranging from C6 – C10. Purified natural gas is odorless and colorless, but sometimes odorants are added for safety and leak detection [2]. Increased natural gas extraction based on directional drilling and hydraulic fracturing stimulation technologies has generated concerns about the

contamination of drinking water and other environmental problems. Methane has limited solubility in water and can be flammable when vented to the atmosphere. There are two different types of methane produced naturally – biogenic methane and thermogenic methane. Biogenic methane is produced at shallow depths as a byproduct of bacterial metabolism. Thermogenic methane is formed by geological processes at depths exceeding 1,000 m as a function of high temperature and pressure. In the latter, the decomposition of organic materials into methane gas and heavier saturated components (C2 – C4 hydrocarbons) creates a signature that can be used to discern between thermogenic and biogenic sources. Thermogenic methane is also the primary target of unconventional natural gas extraction. Prior research has shown instances of very high methane concentrations in water. Some were 17 times higher on average in shallow water wells near active drilling and extraction areas than in wells from non-active areas in northeastern Pennsylvania and upstate New York [2]. Such concentration levels are considered hazardous; determining the source of the methane is therefore important in order to devise mitigation strategies [3][4]. Additionally, permanent gases, like methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) are primary contributors to climate change [5]. Small leakages of methane, the major component of natural gas, have been indicated to have greater global warming potential than previously believed, when the indirect influence of methane on atmospheric aerosols are considered [6].

The determination of the hazardous decomposition products from a thermal runaway reaction of lithium-ion and lithium-metal batteries is another important gas analysis application [7]. This is highlighted by the near ubiquitous nature of chemistry of lithium-ion batteries which are used in cell phones, laptops, automobiles, and other portable devices [8]. As a primary source of energy for portable electronic devices, the chemistry in Li-ion batteries can provide the maximum energy density, which is susceptible to thermal runaway when overheated from overcharging or exposed to high temperatures. The decomposition of the anode and cathode results in battery capacity loss and environmental hazards. During transportation of the Li-ion battery, it is possible for an internal short to form, a battery to rupture, for toxic and flammable gases to form, and even a fire to begin. The amount of gas generated can be substantial and can cause very hazardous environmental or health problems. Undesired decomposition from both capacity loss and gas evolution should be carefully analyzed and controlled [9].

At the current pace, lithium demand is expected to increase 18-fold from 165,000 tons per year in 2013 to a minimum of 3 Mt (million tons) per year by 2030 [10]. The global lithium resource is estimated to be about 39 Mt for the period 2010 to 2100. The high growth rate regarding the production and use of lithium has attracted attention about assessment of environmental and safety concerns. In May 1999, the International Power Sources Symposium proposed an amendment about transportation of dangerous goods – lithium-ion batteries. Concerns regarding the transportation of lithium-ion batteries have since appeared in more regulations [11]. Many fires and explosions have been reported throughout the world during the past years. The flammability of the electrolyte, the rate of charge and/or discharge, and the engineering of the battery pack provide various levels of concern. In some cases, greater instability is accepted as a consequence of higher performance products [2, 12]. These risk factors need to be assessed.

Gas chromatography has continuously played an important and reliable role in gas analysis and that has no tendency to fade away [13]. Good selectivity and sensitivity of separation is tightly related to column chemistries, sample introduction techniques, and detectors [14]. Porous-layer open tubular (PLOT) columns, first suggested by Golay in the late 1950s, are used in many contemporary applications of GC, and are considered to be a worthy alternative to packed columns. Compared to packed columns, PLOT columns provide better efficiency, greater resolution, and faster separations; collectively, these have extended their application to a wide range of fixed gases, light hydrocarbons, and volatile solvents [15]. Additionally, compared with the most common liquid stationary phase wall-coated open tubular (WCOT) columns, PLOT columns exhibit more retention of volatile compounds and permanent gases at sub-ambient and super-ambient oven temperatures, and thus facilitate better qualitative and quantitative abilities for these analytes [16].

Over 60 detectors have been designed for GC application since the inception of the technique. These include the well-known flame ionization detector (FID), thermal conductivity detector (TCD), electron capture detector (ECD), and mass spectrometer detector (MSD). However, not all of them are suitable for the analysis of permanent gases or highly volatile compounds. FID and ECD are considered as selective detectors that only detect compounds with specific chemical, physical, and molecular

properties. For example, while FID provides high sensitivity and wide linear range, it only detects compounds containing organic carbons. ECD only detects compounds with high electron affinity, therefore it is often used for selective detection of halogenated compounds. TCD, on the other hand, is a universal detector; however, the sensitivity of the TCD is generally orders of magnitude worse than other detectors [17]. Even though many official standardized methods rely on MSD technology, because of its excellent sensitivity for trace quantitative analysis and capability for identification of analytes of interest, it has significant limitations for the detection of low mass compounds typically encountered in gas analysis.

To address these limitations, a vacuum ultraviolet (VUV) detector has been recently introduced [14]. Gas chromatography with VUV detection (GC-VUV), has been presented as an alternative tool for GC-MS, and it has been demonstrated for the analysis of hydrocarbons, polyaromatic hydrocarbons, fatty acids, pesticides, drugs, and estrogens. GC-VUV provides universal detection through full wavelength range absorption measurements in the 115-240 nm range. All chemical compounds absorb in this wavelength region and have unique and highly featured absorption spectra. Analytes eluting from the GC are passed through a heated transfer line, mixed with a make-up gas, and enter the flow cell (10 cm path length; 80 µL volume). The make-up gas flow can be varied to optimize residence time in the cell, and to avoid band broadening. The absorption of VUV light, provided with a deuterium source module, is monitored using a charge coupled detector at a rate of up to 100 Hz.

The aim of the study is to demonstrate the use of GC-VUV for analysis of permanent gases from sources of high relevance to the modern world and energy industry. Included are applications to natural gas characterization, the analysis of natural gas in the headspace of collected groundwater, and the evolution of gases from thermal runaway events in Li-ion and Li-metal batteries. GC-VUV is shown here to provide reliable detection of gaseous (and other volatile/semi-volatile) components in these applications. The detector can be used to fully deconvolute co-eluting species based on known absorption cross-sections for the different analytes.

3.3 Experimental

3.3.1 Instrumentation

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instrument, Inc., Columbia, MD) was coupled to a VGA-100 VUV detector (VUV Analytics, Inc., Austin, TX) and used to collect data from a variety of gas samples. The data collection rate was set at 10 Hz. The transfer line and flow cell temperatures were set at 300 ^{o}C and 275 ^{o}C, respectively, and the make-up gas (argon) was set to 0.25 psi. While make-up gas reduces the residence time of the analyte in the flow cell and thus its signal, we nevertheless found that the set pressure of 0.25 psi was more than sufficient for this application. The column used was an HP PLOT/Q (30 m x 0.32 mm x 20 µm) from Agilent Technologies (Santa Clara, CA) and it was operated in the constant velocity mode (27 cm.s^{-1}) with helium carrier gas.

The oven profile for natural gas application was set to start at 50 ^{o}C (held for 4 minutes) and then increased to 200 ^{o}C at a rate of 15 ^{o}C/min (held for 5 minutes). The injection port was operated with a split ratio of 20:1. The oven profile for Li batter off-gasing application was set to start at 40 ^{o}C (held for 7.85 minutes) and then increased to 250 ^{o}C at a rate of 5.7 ^{o}C/min (held for 7 minutes). The injection port was operated with a split ratio of 5:1. The injection port temperature was set at 250 ^{o}C. Manual injection was performed. The injection volume varied depending on application.

3.3.2 Natural Gas Standard

A natural gas standard containing nitrogen, carbon dioxide, methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, and hexanes+EX6 was obtained from DCG partnership (Pearland, TX). The composition of the standard is shown in Table 1.

Table 3-1 Concentration of different components in a natural gas standard

Components	Concentration (mole %)
Nitrogen	1.005%
Carbon Dioxide	0.503%

Methane	94.720%
Ethane	2.013%
Propane	0.753%
iso-Butane	0.302%
Butane	0.301%
iso-Pentane	0.151%
n-Pentane	0.151%
Hexanes+EX6	0.101%

3.3.3 Sample collection

Water samples containing natural gas were collected from Parker County in the Barnett Shale formation of north Texas. These samples were obtained from water wells that are located less than a mile from an unconventional gas well where hydraulic fracturing was used for stimulation. Water from these wells has been shown to be flammable, indicating dissolved methane concentrations above 20 mg/L.

Water samples were collected through a chemical-free hose in which the sample passed through a 25 gauge needle into a 50 mL glass serum vial sealed with a thick rubber septum. During collection, another needle was pressed through the rubber septum to act as a release for the headspace and any bubbles that formed. Upon filling the bottle and purging all of the bubbles, water was cycled through the bottle for at least 4 bottle volumes. Once the appropriate time had elapsed, the purging needle was removed, then the source needle, and the septum maintained an air-tight seal. Upon receipt, samples were refrigerated upside down in the lab. During storage, a small headspace volume evolved. For analysis, the sample was kept inverted and 5 mL helium was introduced through an 18-gauge needle while 5 mL of water was withdrawn through an 18-gauge needle fitted to a syringe. The sample was then

vortexed thoroughly, sonicated for 10 s, and then equilibrated to room temperature. Following this, 0.300 mL of the headspace was injected using a 1 mL Pressure-Lok VICI gas tight syringe.

Li-ion and Li-metal battery samples were obtained commercially, and included lithium-cobalt-oxide (LCO; CO), lithium-nickel-manganese-cobalt-oxide (LMnNiCO; NMC), and lithium-manganese-nickel (LMnNi; MN) 18650 cells (18 mm diameter and 65 mm length).

The off-gassing from batteries was collected using a specially designed chamber, which was used to contain the reaction and guide the expended gaseous byproducts to a 1L multi-layer foil gas sampling bag from Restek Corporation (Bellefonte, PA), as shown in Figure 1. The chamber was constructed to contain the reaction and to collect thermal and gas flow data. The chamber has a stainless steel pipe with a connecting t-junction and a cap on both ends. As shown in Figure 1A, a length of heating tape was wrapped around the test chamber as a heat source to induce a thermal event and cause thermal runaway. A minimum of 100 ^{o}C/min heat rate is needed in order to cause thermal runway. While one end of the t-junction is capped, the other end is connected with a Swagelok fitting through which the reaction gas flows. The gas was collected in multi-layer foil gas sampling bags (Figure 1B) a suitable length of distance away from the reaction chamber to allow cooling of the gas products. Following collection, 0.500 mL samples from the sampling bags were withdrawn to be injected in the GC-VUV using a 1 mL Pressure-Lok VICI gas tight syringe. Figure 1C shows a photograph of a LCO cell after the experiment was complete.

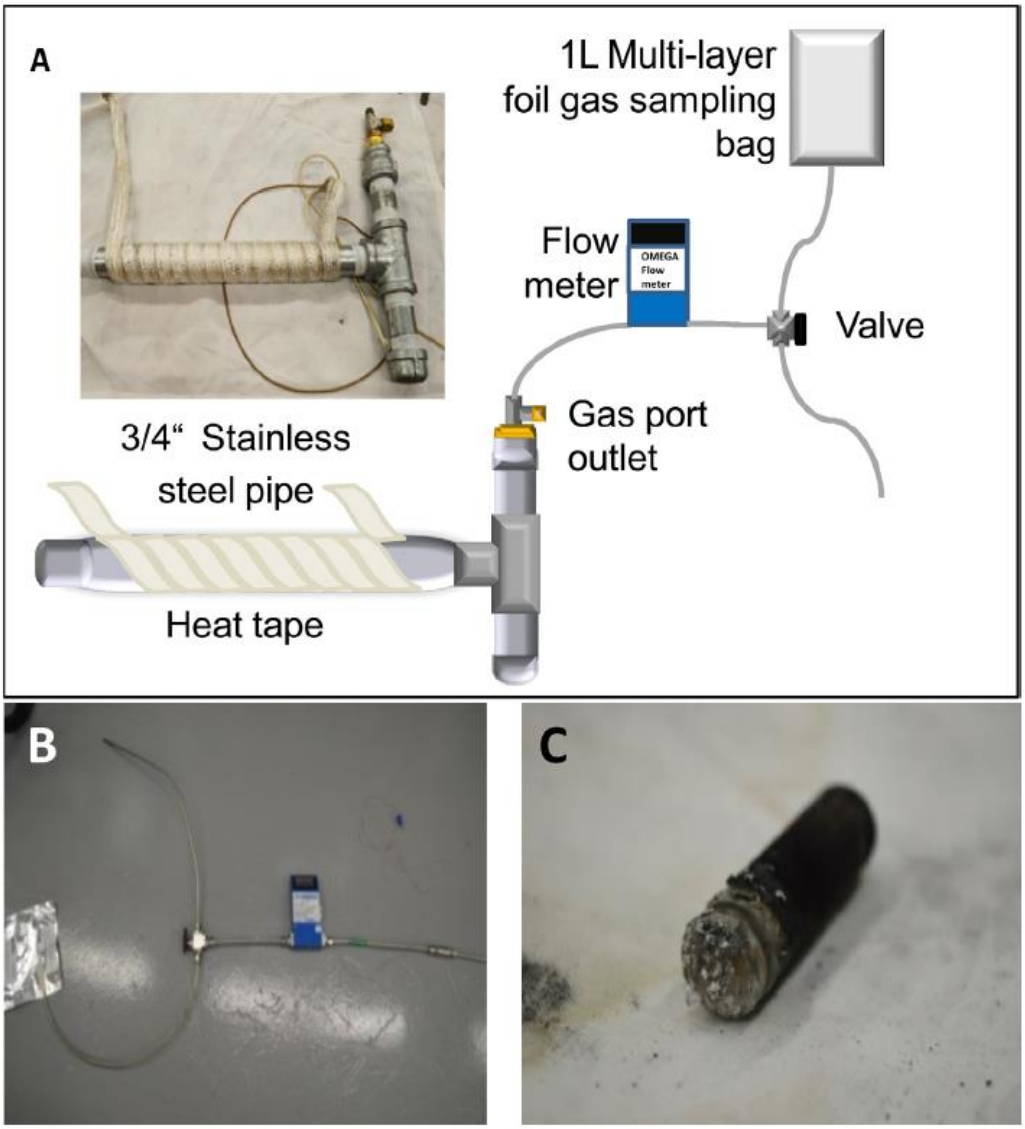

Figure 3-1 Generation and collection of gases from thermal runaway of 18650 Li-ion and Li-metal batteries includes a stainless-steel test chamber setup with heat tape (A) and a gas collection line and sampling bag (B). An LCO cell post-test is shown in (C).

3.3.4 Data Analysis and Deconvolution

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

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

In Eq. 1, d is the flow cell length and V is the flow cell volume. There is one equation like this at each wavelength value j. Removing the subscript j allows generalization of the wavelength dependence of absorption:

$$A = \frac{1}{\ln(10)} \frac{d}{V} \left(\sigma_1 N_1 + \sigma_2 N_2 + \ldots + \sigma_n N_n \right) \qquad \text{Eq. 2}$$

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 are the cross section tables contained in the VGA-100 spectral library. 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 $\frac{1}{\ln(10)} \frac{d}{V} \sigma_i$ are the basis functions to be used in the linear optimization procedure (i.e., the fit procedure).

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

$$A = \sum_{i=1}^{n} f_i A_{i,ref} = \left(f_1 A_{1,ref} + f_2 A_{2,ref} + \ldots + f_n A_{n,ref} \right) \qquad \text{Eq. 3}$$

Here, the f_i are the parameters to be optimized and the $A_{i,ref}$ are the basis functions. The advantage of 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 [18].

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

Eq. 2 or Eq. 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 ith component relative to the ith 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.

3.4 Results and Discussion

3.4.1 Natural gas standard analysis

There are a number of reasons why natural gas analysis is important, including sourcing and quality control [19]. Early on, gas chromatography equipped with TCD and FID has been used widely in separation and measurement of natural gas [20]. TCD is typically used to measure nitrogen, carbon dioxide and light hydrocarbons, whereas FID is often utilized to the determination of higher hydrocarbons [2].

Using GC-VUV, all of these components can be measured at once. Figure 2 shows the separation and detection of components in natural gas standard using the HP-PLOT Q BOND column on the GC-2010 coupled with the VUV detector. The peaks indicated in the figure were identified based on matches with library spectra. Also shown are the library absorption spectra for some of the components. The variety in spectral features is apparent. It is also worth noting that the spectra for other linear hydrocarbons match qualitatively that shown for methane. However, longer n-alkanes exhibit higher molar absorptivities in the low wavelength range (115 – 150 nm).

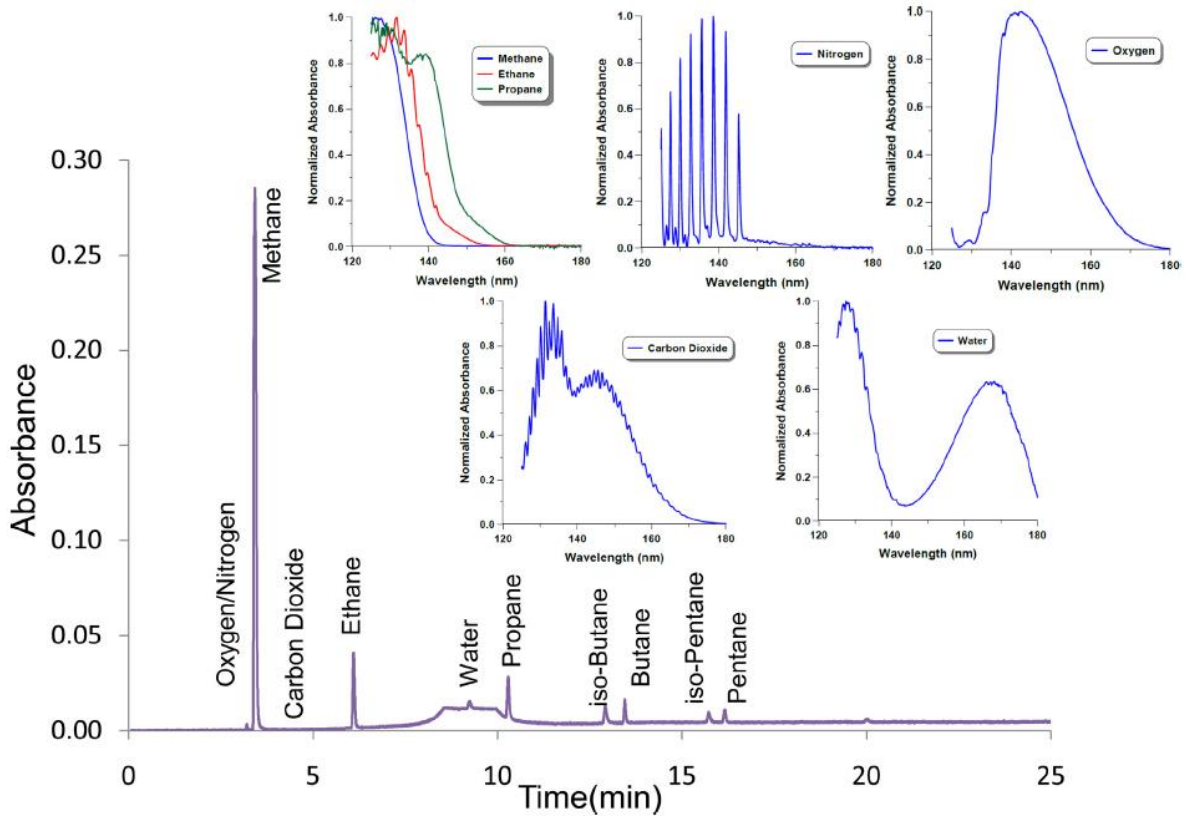

Figure 3-2 GC-VUV chromatogram of natural gas standard based on absorption from 125-240 nm. Representative spectra used to identify some of the analytes are shown.

3.4.2 Natural gas in water analysis

Figure 3 shows overlaid chromatograms of three water headspace samples. The results show us that the water sample headspace contains a very similar composition to the natural gas standard (Figure 2). Furthermore, because the C2 – C4 hydrocarbons are not produced biogenically, the water has been likely contaminated by natural gas of a thermogenic origin. The primary difference noted in the overlaid chromatograms is the larger abundance of water in the headspace samples, which is expected. While quantitation of the natural gas components in the water samples could be pursued, it is beyond the scope of this study. The quantitation is complicated by the general need to have available standards for calibration. Introduction of the standards into water samples to mimic the distribution of dissolved and

headspace gases will require further development and refinement to achieve appropriate reproducibility. While the VUV detector is capable of direct pseudo-absolute quantitation of the number of molecules in the detector (based on the available library cross sections for analytes) [14], the multi-phase sampling and introduction of sample into the GC instrument would require a comprehensive assessment of potential sample losses. Some further calibration or internal standardization would still be necessary.

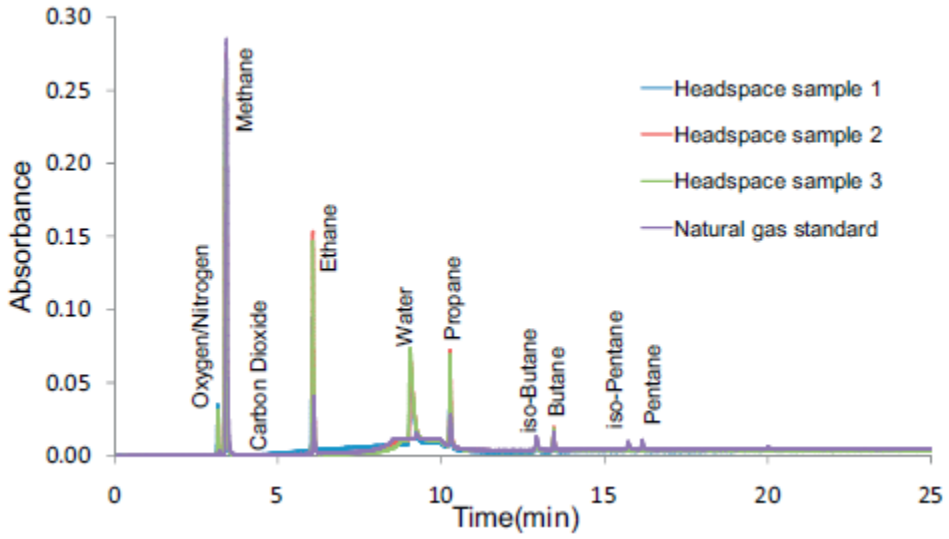

Figure 3-3 Overlaid GC-VUV chromatograms of water headspace and natural gas standard sample based on absorption from 125-240 nm.

3.4.3 Thermal decomposition of Li-ion and Li-Metal batteries

Figure 4 shows overlaid chromatograms of different types of Li-ion and Li-metal battery from thermal runaway off-gassing. Significant quantities of volatile gases have been captured, including those that are flammable (e.g., methane, ethylene, and propene) and toxic (e.g., acetaldehyde, 1,3-butadiene, and chloromethane). The chromatogram shows generally good resolution of the components of the mixture on the PLOT column. However, there are a couple of instances where coelution is apparent. It is well known that carbon monoxide and oxygen co-elute on a PLOT/Q column. These components are key decomposition products in the study of thermal runaway reactions of Li-ion batteries. Ordinarily this

requires a TCD (or equivalent) detector and the use of a different PLOT column, such as a PLOT 5Å molsieve or Carboxen-1010, to afford resolution. GC-MS is not capable of resolving the relative contribution of these signals when they co-elute. The use of alternative column technologies relies on stronger adsorption mechanisms to separate oxygen and carbon monoxide and would entail excessive retention for the remaining compounds found in the failed battery gas sample. Here the power of the VUV detector and software is exhibited in the deconvolution of these two co-eluting analytes.

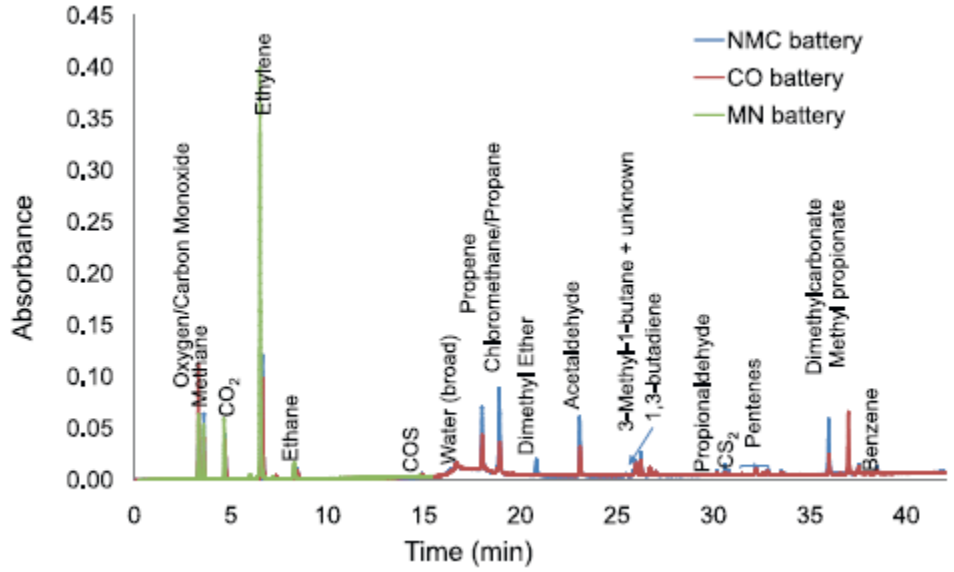

Figure 3-4 Overlaid GC-VUV analysis of three different lithium-ion battery samples. Gas samples were collected from LCO, LMnNiCO, and LMnNi 18650 cells using the apparatus depicted in Figure 1.

A magnified view of the NMC battery chromatogram from Figure 3-4 is shown in Figure 3-5. The right inset shows the measured ("Original") absorption spectrum at the peak maximum. The VUV spectrum for oxygen consists largely of a broad hump spanning approximately 130 – 175 nm. The VUV spectrum for carbon monoxide spans a similar range (130 – 156 nm) but consist of at least nine sharp vibrational features. The stark difference in spectral features for these two analytes allows for their efficient deconvolution. The relative contribution of oxygen and carbon monoxide can be deconvolved,

and when combined with the background noise, the original chromatographic response can be reconstructed based on the summed contribution of each component to the measured signal.

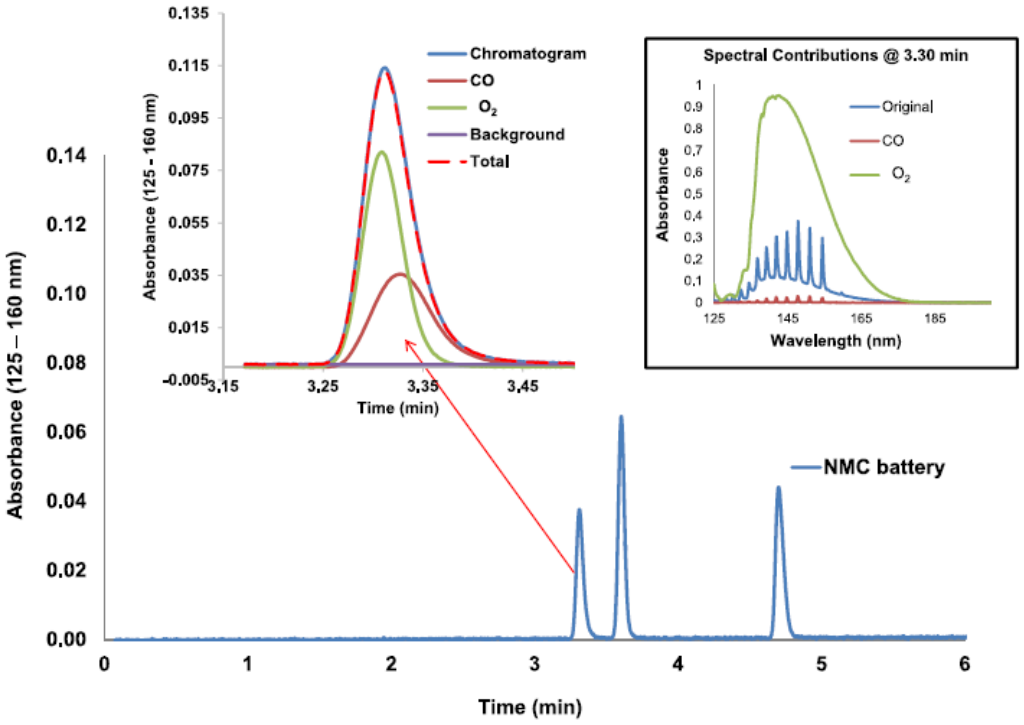

Figure 3-5. Deconvolution of coeluting CO and O_2 chromatographic signals from the off-gassing of the NMC battery sample.

A similar example is exhibited in Figure 6. Here, propane partially overlaps with the larger chloromethane peak, both of which lie on top of a broad water peak. On the left is shown the spectral contributions of the three analytes at the peak apex (19.0 min). On the right is shown the individual contributions to the measured composite sample, and the reconstructed chromatogram based on the sum of individual absorbance signals. Again, the spectral features are distinct and the three analytes could be easily decoupled from one another.

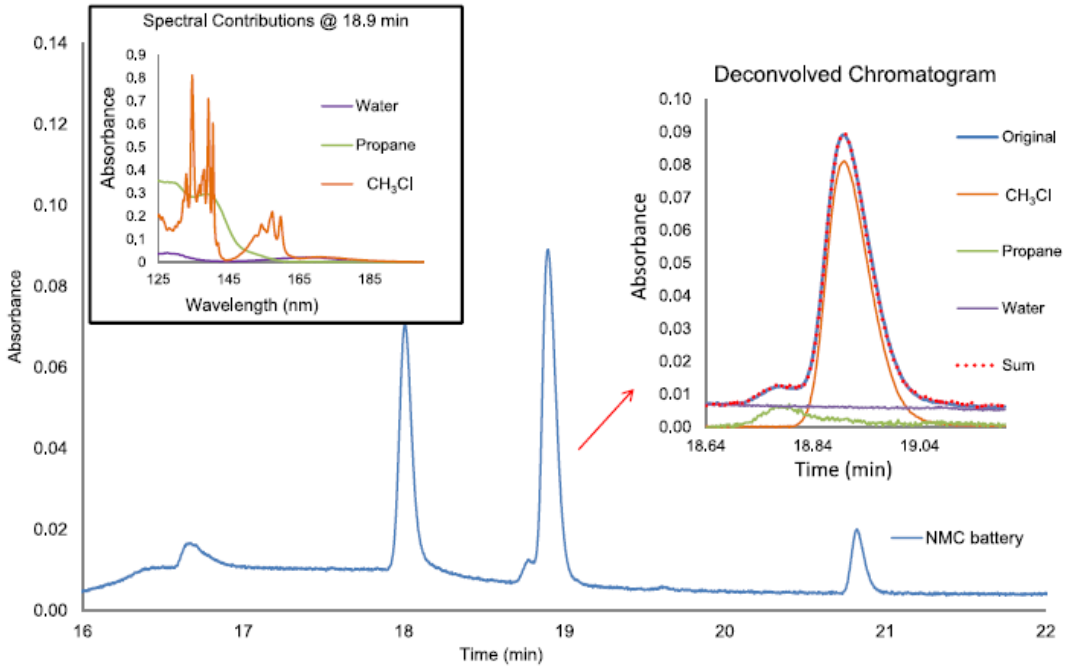

Figure 3-6. Deconvolution of coeluting propane, CH_3Cl, and water chromatographic signals from the off-gassing of the NMC battery sample.

3.5 Conclusion

Two gas analysis applications have been described using a GC-VUV instrument. In the contamination of drinking water by natural gas, it was shown that all signals could be associated with thermogenic methane. This preliminary determination does not involve quantitative analysis, although efforts associated with this capability has been initiated and will be reported in a separate communication. It will be important to precisely account for losses and variability due to sample collection and then sampling of the vial for introduction into the instrument. To demonstrate the potential for universal detection of a wider range of chemical compounds, gas production during thermal runaway of decomposing Li-ion and Li-metal batteries was evaluated. No other GC detector can easily delineate and determine the relative contribution of components present in overlapping chromatographic signals. In this way, the VUV detector is quite unique, but it also provides much of the capability for compound identification that users generally expect from GC-MS. As the compound library continues to be

expanded, so will the capability of GC-VUV for solving challenging analytical problems related to permanent gases, as well as volatile and semi-volatile compounds.

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Chapter 4

Comparison of GC-VUV, GC-FID, and Comprehensive Two-Dimensional GC-MS for the Characterization of Weathered and Unweathered Diesel Fuels

4.1 Abstract

Characterization of diesel fuels and degraded diesel fuels in the environment is a common issue nowadays. Providing definitive information for litigation regarding determination and distinguishing the origins or sources of fuel spill contamination has been a significant need among the environmental forensics community. Diesel fuels contain more complex chemicals and isomers compared to gasoline. Here, we compare the use of gas chromatography – vacuum ultraviolet spectroscopy (GC-VUV) and comprehensive two-dimensional gas chromatography – mass spectrometry (GC×GC-MS) for diesel fuel and weathered diesel fuel analysis in fingerprinting biomarkers. GC-VUV is a relatively new technique that can rapidly acquire full absorption spectra from 120-240 nm. Class information about individual components is readily obtained based on reference to a library of matched spectra. Direct comparison of GC-VUV, GC-FID, and GC×GC-MS was undertaken to identify different classes of compounds and biomarkers. Using GC-VUV, numerous peaks representing minor and major components were classified into different classes by applying spectral filters and, in some cases, spectral deconvolution. Isoprenoid biomarkers, such as pristane and phytane, and their ratios with n-alkanes, C_{17} and C_{18}, respectively, were determined The biomarker ratio results from GC-VUV matched well with both 1D GC-FID and 2D GC-MS. About 5%-20% difference in measured biomarker ratios were obtained for a series of commercial weathered diesel standard samples, which is good enough to allow the discrimination of different weathered diesel samples.

4.2 Introduction

Crude oil was formed over a span of millions of years from buried dead and decaying plants and animals that were exposed to high temperatures and pressures in a hypoxic environment. Once extracted from the ground, it can be refined into numerous different types of high value fuels and petrochemical

products [1]. Crude oil predominantly contains different classes of hydrocarbons and other chemical compounds. Due to the presence of different temperatures, pressures, and source materials during formation, crude oils obtained from different locations have significantly different chemical signatures. Many different fingerprinting techniques have been reported to visualize these differences [1,2,3,4].

Diesel fuel is a high volume refinery product distilled from crude oil. It contains more complex chemical components than gasoline, ranging approximately from C_{10} to C_{22} and including many different isomeric species [5]. The most abundant compounds can be classified into four major hydrocarbon groups, namely paraffins, isoparaffins, naphthenes, and aromatics. The relative abundances of these groups of compounds are very useful for comparing samples of known origin to those from suspected contamination events [6].

Because of the high power-efficiency and economical features of diesel fuel, worldwide demand is very high. Along with the need to transport large volumes of diesel fuel, there exists significant potential for spills into the environment. Diesel fuel spills in soil from leaking underground storage tanks, pipelines, and accidents can cause groundwater contamination and can be toxic to soil microorganisms and plants [7]. Diesel fuel is one of the most acutely toxic oil types; spills can threaten natural marine resources, wildlife, and habitats [8,9]. Therefore, identifying and characterizing diesel spills, and linking them to suspected sources, is an important part of environmental forensics investigations. Fingerprinting multiple classes of compounds and analyzing biomarkers are the most popular methods used [2,10]. Many methods have been developed to analyze diesel fuels; however, there is no perfect routine method that can be applied to fully and readily satisfy the objectives of related forensics investigation [2,11].

Several different classes of compounds in diesel fuel, including alkanes, cycloa]lkanes, alkylbenzenes, alkylnaphthalenes, and anthracene/phenanthrenes, are primary targets for source and age identification measurements [2,6,12]. n-Alkanes like C_{17} and C_{18} are the highest abundance compounds in fresh diesel, and isoprenoids are the most predominant in weathered and biodegraded diesel; thus, their ratios can be used to determine the degree of the diesel degradation, the age of a diesel spill, and help to identify the source of spilled diesel [1,13]. Pristane and phytane are the two isoprenoids that serve as biomarker indicators in diesel fuels because of their large abundance and ease of measurement [14,15,16]. Steranes, hopanes, and triterpanes can be useful biomarkers in petroleum

analysis but are less abundant in diesel fuels [12]. Biomarkers further play an important role in oil exploration; however, their presence in complex petroleum mixtures is very low, which makes them difficult to detect [17,12].

Overall, there are several technical challenges with diesel fuel fingerprinting. First, target compounds used to identify suspected sources of the spill can be hard to determine since they can undergo several weathering processes that could change the composition of the oil. These include evaporation, emulsification, dispersion, biodegradation, and photooxidation, among others [2,4]. Second, developing a routine procedure with appropriate detection limits to collect sensitive and high resolution data over time is very important, but not easy to achieve [3].

One-dimensional gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detection are the most popular methods for fuel forensics; they have been widely applied because they can provide fundamental information for major components. However, when it comes to detailed minor compounds, they may not provide sufficient resolution [18]. Other methods developed for petroleum analysis have featured techniques such as high-performance liquid and supercritical fluid chromatography, as well as infrared, ultraviolet, fluorescence, and nuclear magnetic resonance spectroscopy [4,19]. However, because of the inherent complexity of the sample matrix, none of these methods can provide a comprehensive analysis of diesel fuel.

Comprehensive two-dimensional gas chromatography (GC×GC) with FID and with MS has also been applied for characterization of diesel and weathered diesel samples [20,21,22]. GC×GC can provide very detailed information about the various sample constituents due to its potential for increasing peak capacity by an order of magnitude versus one-dimensional GC. It also provides significant insight into the presence of various compound classes, since the signatures of these classes are highly ordered in the GC×GC contour plot [6,23]. However, there are some limitations to GC×GC. GC×GC can be less user-friendly and relatively harder to operate and maintain because of additional hardware and software requirements. Method development challenges include the optimization of the modulator, it's modulation time, and the avoidance of wrap around. In addition, the capital equipment and maintenance costs can be quite high. For environmental forensics, these benefits can surely assist law enforcers to solve problems, but it can be difficult for forensic chemists, since they must communicate results to a non-scientific

audience (e.g., lawyers and judges), and they may not be experts in chemometrics or GCxGC [11,23,24]. Even though advancements in availability and capability of instrumentation and software have been made for GCxGC, one dimensional GC is a much more widely understood and accepted technique in the general and environmental forensics fields.

Vacuum ultraviolet spectroscopy, which has universal detection capabilities [25], coupled with gas chromatography (GC-VUV), has been applied in this research to demonstrate the possibility of its use for resolution of different compound classes and direct speciation of target biomarker compounds in complex diesel samples. Vacuum ultraviolet spectroscopy has been shown to address some limitations of other GC detection techniques due to its added spectral resolution, deconvolution, and quantitative capabilities [25,26,27]. Various applications have been previously demonstrated using GC-VUV, including those related to permanent gases [26], fatty acid esters [28,29], multiclass pesticides [30], terpenes [31], dimethylnaphthalene isomers [32], and gasoline compound class speciation analysis [33]. Of particular note, the latter work on gasoline compound speciation features a new means for PIONA analysis based on the use of time interval deconvolution (TID). However, diesel fuel is far too complex to currently allow for automated speciation as was performed for gasoline. The VUV spectral library does not yet contain many of the more complex hydrocarbon species present in diesel fuel that would enable such an analysis. That said, researchers have applied GC-VUV and GC×GC-VUV to explore some compound classification in diesel fuels previously [32,34,35].

The aim of this study was to utilize the unique features of GC-VUV to differentiate and characterize classes of compounds, specifically to fingerprint common biomarkers for age and source identification, in a series of commercial unweathered and weathered diesel fuels. Further, results were compared to those obtained using GC×GC with time-of-flight (TOF) MS, as a means to evaluate different state-of-the-art technologies. By applying different VUV spectral filters, normal alkanes, monoaromatics, and substituted naphthalenes were classified into their respective groups. Dimethylnaphthalenes were also targeted for deconvolution using VUV spectra. Meanwhile, isoprenoid biomarkers pristane and phytane and their ratios relative to C_{17} and C_{18} n-alkanes in the different diesel fuels were determined. Good agreement was observed between results obtained by GC-VUV and GC×GC-TOFMS.

4.3 Experimental

4.3.1 Instrumentation and Materials

A composite (unweathered, 0%) diesel fuel, as well as 25%, 50% and 75% artificially weathered diesel fuels and a fuel oil degradation mix, which contained heptadecane (C_{17}), octadecane (C_{18}), pristane, and phytane, were obtained from Restek Corporation (Bellefonte, PA). It is worth noting that the commercially obtained 25%, 50%, and 75% diesel fuels were prepared artificially through evaporation, and that they were not all prepared from the same initial diesel fuel sample. An n-alkane standard mixture from C_7 to C_{40} and a n-hydrocarbon mix (C9 and even number hydrocarbons from C_{10} to C_{36}) were also obtained from Sigma-Aldrich (St. Louis, MO). Response factors were determined for heptadecane (C_{17}), octadecane (C_{18}), pristane, and phytane using the fuel oil degradation study above for quantitative determination of biomarker ratios.

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia MD) coupled to a VGA-100 VUV detector (VUV Analytics, Inc., Cedar Park TX) was used to collect GC-VUV data. A Shimdzu GC-17A GC/FID was used to collect GC-FID data.

The column used for GC-VUV was an Rxi-1ms (30 m × 0.25 mm × 0.25 µm) from Restek and SHRXI-5MS (30 m × 0.25 mm × 0.25 µm) for GC-FID from Shimadzu. Both systems was operated in the constant velocity mode (1.4 mL/min) with helium carrier gas. The GC inlet temperature was set to 275 °C. The injection volume and split ratio were varied for different samples. The GC oven profile was set to start at 40 °C (held for 0.1 min) and then increased to 320 °C at a rate of 6.5 °C/min (held for 5 min). The transfer line and flow cell temperatures for the VUV detector were set to 300 °C, and the make-up gas (nitrogen) pressure was set to 0.25 psi. The data collection rate was set to 2.67 Hz, an acquisition rate that allowed sufficient sampling of each chromatographic peak using the applied GC method.

A LECO Pegasus 4D GC×GC-TOFMS incorporating a dual-stage quad-jet cryogenic modulator and independently-controlled secondary GC oven was used for GC×GC work. Two columns from Restek used for GC×GC were an Rxi-1ms (60 m × 0.25 mm × 0.25 µm) in the first dimension and a Stabilwax (1.1 m × 0.25 mm × 0.25 µm) in the second dimension. Columns were connected using a defined press-fit (deactivated) from BGB Analytik USA, LLC (Alexandria VA). The carrier gas used was helium at a constant flow of 1.4 mL/min. The modulation period was 2.5 sec with a hot-pulse-time of 0.75 sec and a

cool-time-between-stages of 0.50 sec. The thermal modulator temperature offset relative to the primary GC oven temperature was 25 °C. The oven profile for the first-dimension GC was set to start at 40 °C (held for 0.2 min) and then increased to 250 °C at a rate of 2.9 °C/min (held for 7.4 min). The oven profile for the second-dimension GC was operated at a 10 °C offset from the first-dimension program during the entire run. One microliter injections were made into a 250 °C GC inlet containing a 4 mm Restek Sky Precision liner with quartz wool. The split ratio was 50:1. Mass spectra were collected from m/z 45 to 450 at 200 spectra/sec with electron ionization at 70 eV and a source temperature of 225 °C. GC×GC-TOFMS hardware control, data processing, data review, and chromatogram visualization were performed with LECO ChromaTOF software.

4.3.2 Data analysis and VUV spectral deconvolution

Since similar compounds exhibit similar absorbance features, VUV can qualitatively visualize the information according to defined wavelength regions called spectral filters. While this qualitative classification does not match the quantitative chromatographic classification of GCxGC, the interferences from other classes of compounds in GC/VUV can be diminished and sometimes eliminated altogether. As depicted in Figure 4-1, spectral filters from 125 nm to 155 nm, 170 nm to 195 nm, and 200 nm to 230 nm are those where saturated hydrocarbons (octane, pristane, phytane), monoaromatics (benzene, toluene), and diaromatics (naphthalene, 1,5-dimethylnaphthalene) preferentially absorb, respectively. As such, these were used to classify saturated hydrocarbons, monoaromatics, and substituted naphthalenes in diesel fuels and to compare them with the results from GCxGC-TOFMS.

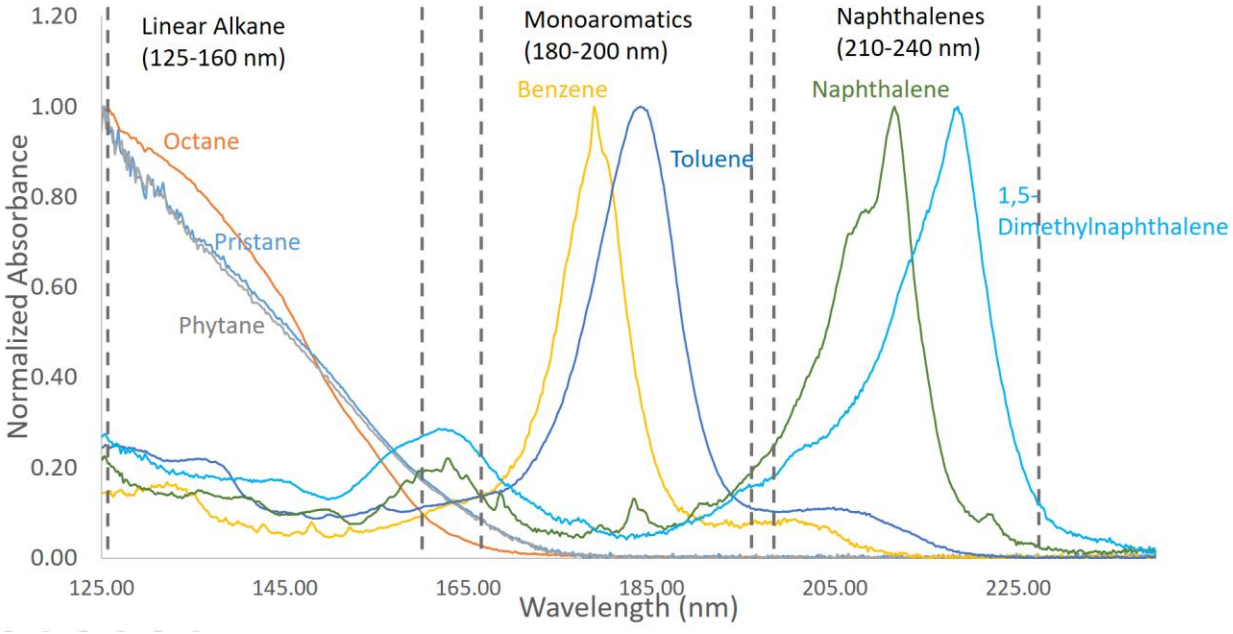

Figure 4-1 Spectral filters were defined to selectively project and visualize a region of the VUV spectrum corresponding to different compound classes, including saturated hydrocarbons, monoaromatics, and diaromatics. These can be monitored real time or extracted post-run from the GC-VUV chromatograms.

In many cases, compounds that have similar properties and isomers will coelute, which makes it more difficult to speciate individual components. Using GC-VUV, the absorption of overlapping signals is additive, and the individual contribution of each component can be easily deconvolved and projected as a separate peak, provided that reference library spectra are available for each of the coeluting species and they are distinct.[26,30] Such analyses was performed using the VUV Model & Analyze software.

4.4 Results and Discussion

4.4.1 GC-VUV characterization of weathered and unweathered diesel fuels.

Weathered and unweathered diesel fuels were analyzed by GC-VUV. Figure 4-2A shows the GC-VUV chromatogram of an unweathered (0%) composite diesel fuel. Figures 4-2B, 2C, and 2D show the GC-VUV chromatograms of the 25%, 50%, and 75% weathered diesel fuels, respectively. The 75%

weathered diesel fuel was characterized by a greater abundance of heavy hydrocarbons due to the weathering process (in this case, evaporation), which reduced the amount of lighter hydrocarbons. Likewise, the 50% weathered diesel fuel had more heavy hydrocarbons and less light hydrocarbons than the 25% weathered diesel fuel, and the 25% weathered diesel fuel had more heavy hydrocarbons and less light hydrocarbons than the unweathered composite diesel fuel. In the VUV chromatograms, different spectral filters, which include 125-155 nm (for saturates), 170-195 nm (for monoaromatics), and 200 – 230 nm (for diaromatics), were used to preferentially project the presence and relative abundance of these compound classes. Notable is the presence of a group (C18:1, C18:2, and C18:3) of long chain, unsaturated fatty acid methyl esters (biodiesel), only in the 0% and 50% (Figures 4-2A and 4-2C, respectively) samples, which are accentuated using the 170-195 nm spectral filter between 29 and 30 minutes in the chromatograms.

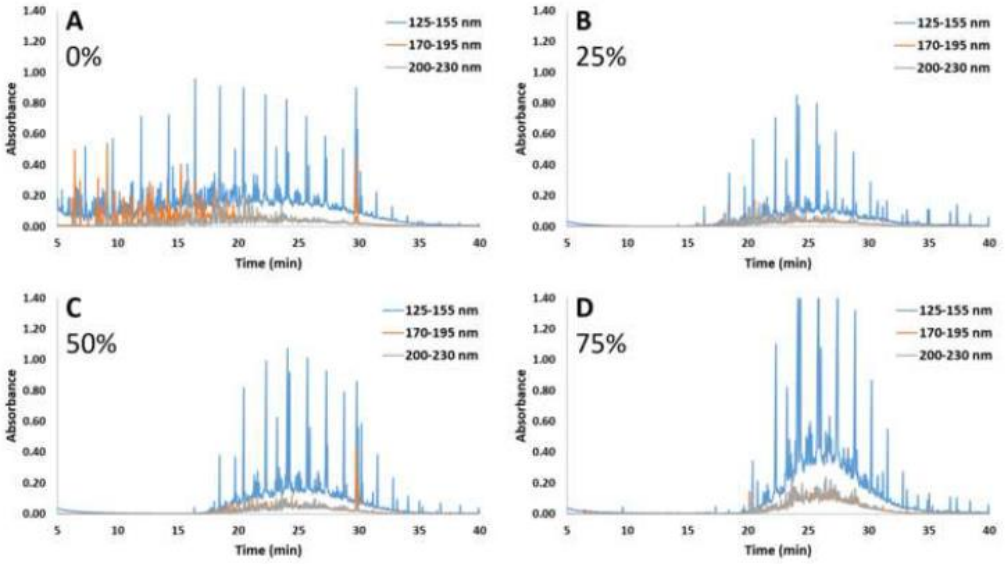

Figure 4-2 Chromatograms with applied spectral filters for GC-VUV analysis of (A) unweathered, (B) 25% weathered, (C) 50% weathered, and (C) 75% weathered diesel fuels. The weathered diesel fuels were artificially weathered by evaporation.

By applying the spectral filter from 125-155 nm, one can preferentially view the saturated hydrocarbons from the diesel fuel sample. This is shown more explicitly in Figure 4-3, where the grey chromatogram represents the various alkanes from the diesel sample. For comparison, n-alkane

hydrocarbon standard mixes were analyzed to gauge the position of n-alkanes in the diesel samples. In addition, by applying the spectral filter for saturates, pristane and phytane were easily located in the chromatogram, a fact that was used later for biomarker ratio determination. Figure 4-3 also shows the spectra of C_{17}, C_{18}, pristane and phytane collected from standards and used to aid in their identification. Such efforts will continue to be necessary in order to build the VUV library to the extent where it can potentially be used for automated compound class speciation in diesel fuel, as was performed previously for gasoline [33]. However, in principle, the complexity of higher carbon species in diesel samples may make it very difficult, if not impossible, to find suitable standards for banking unique spectra for all diesel components, and thus, such classifications may need to rely on the general shapes of absorption spectra in order to group various responses into appropriate bins. Various computational means are also currently being explored to aid this process [25,32].

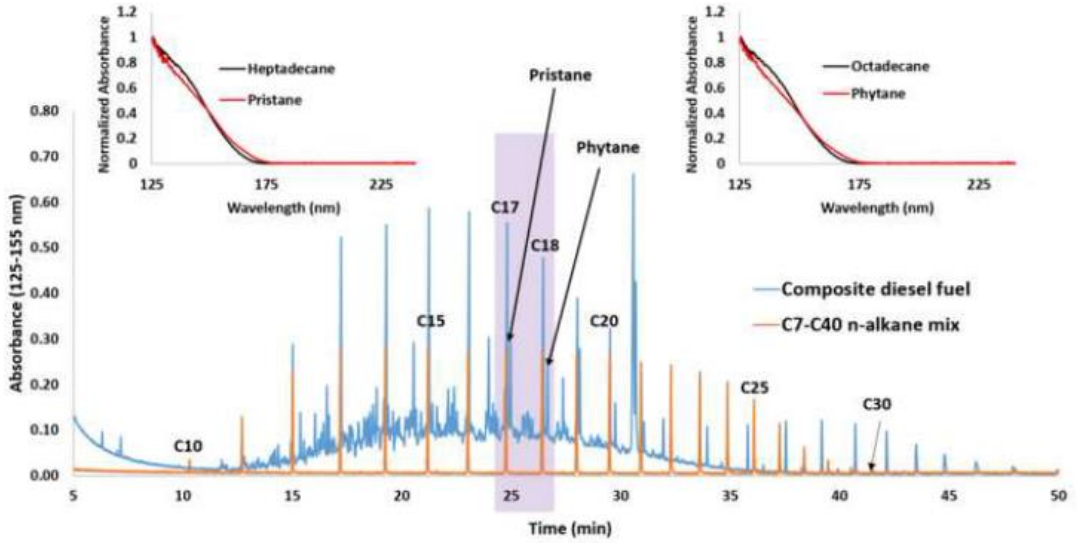

Figure 4-3 VUV visualization and identification of normal alkanes and biomarkers (pristane and phytane) in unweathered diesel through application of the 125-155 nm spectral filter and comparison of retention to an n-alkane standard.

The use of additional spectral filters can aid this speciation in lieu of appropriate standards. As shown in Figure 4-4, monoaromatics can be emphasized using the 170-195 nm spectral filter, and diaromatics can

be preferentially visualized using the 200-230 nm filter. Highlighted specifically are a series of dimethylnaphthalenes and trimethylnaphthalenes in the composite diesel fuel sample. When the response of signals in the 200-230 nm spectral filter exceeds those using the 170-195 nm spectral filter, it provides unambiguous evidence that substituted naphthalenes are present, since they absorb stronger in the longer wavelength region. Such treatments clearly improve the sensitivity and specificity for identification of compound classes having unique absorption signatures.

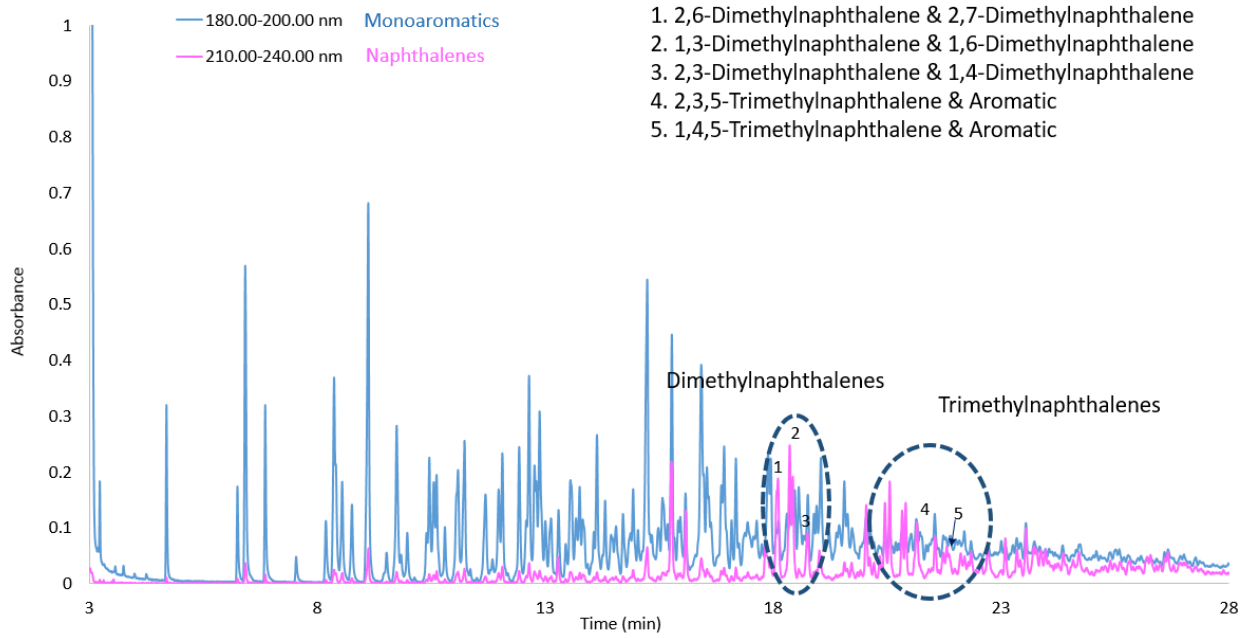

Figure 4-4 Preferential visualization of monoaromatics and diaromatics (specifically, dimethyl- and trimethyl-napthalenes) from unweathered diesel fuel by applying the 170-195 nm and 200-230 nm spectral filters following GC-VUV analysis.

Dimethylnaphthalenes (DMN) and trimethylnaphthalenes are also useful aromatic biomarkers for assessment of maturity and identification of source rock and coals; they might further be good for environmental forensic assessments [16,36,37]. Deconvolution of DMN standard isomers to glean limits of deconvolution using GC-VUV has been demonstrated previously [30]. Here, we evaluated the ability of the instrument to deconvolve DMNs in a real sample matrix. As shown in Figure 4-5, constraining the chromatographic response to the 200 – 230 nm wavelength region, the deconvolution of coeluting 2,6-

DMN and 2,7-DMN, and the deconvolution of coeluting 1,3-DMN and 1,6-DMN from the unweathered diesel fuel was achieved. This selectively targets the absorption feature of naphthalene-type molecules, minimizes the contributions from monoaromatics, and eliminates the contributions from aliphatic and naphthenic compounds (Figure 4-1). The software is designed to elucidate a linear combination of reference spectra corresponding to each of the coeluting compounds in order to calculate their individual contribution to the total signal, thus allowing reconstruction of their individual responses. A residual signal contributing from the background and an overlapping monoaromatic component, which still absorbs to a small degree in this wavelength range, made up the difference in the overall response.

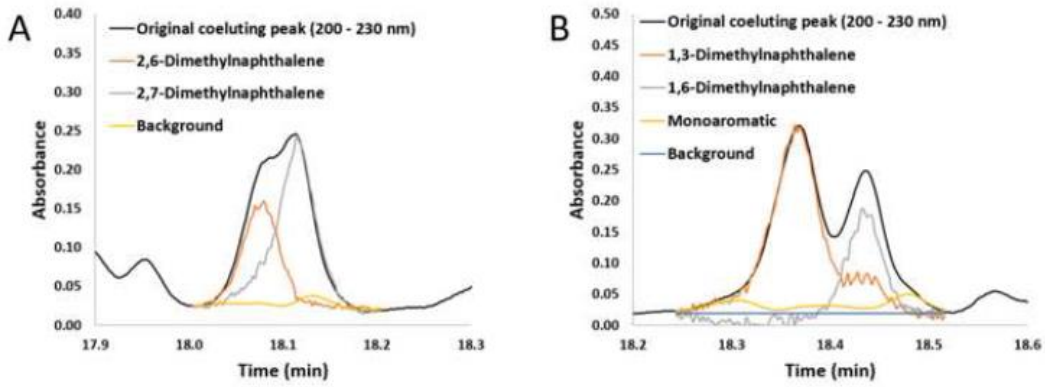

Figure 4-5 Deconvolution of (A) 2,6-DMN and 2,7-DMN and (B) 1,3-DMN and 1,6-DMN with the aid of a 200 – 230 nm spectral filter. Contributing signals from the background and a residual monoaromatic species in (B) were also deconvolved.

4.4.2 GC×GC-TOFMS speciation of weathered and unweathered diesel fuels

Figure 4-6 shows the separation of diesel samples using GCxGC-TOFMS. Figure 4-6A, 6B, and 6C shows the two-dimensional chromatograms as contour plots of the unweathered (0%) composite diesel fuel sample. Aliphatic species are clustered along the first dimension axis due to their limited retention on the polar second dimension column, while aromatics are well retained on the second dimension and moved into the space in the middle of the plot (Figure 4-6A). The aromatic species are distributed in various groups throughout the two-dimensional chromatogram (Figure 4-6B). A closer view

of the aliphatic portion of the chromatogram in Figure 4-6C shows peaks for some biomarkers of interest that are discussed in the next section. Figure 4-6D, 6E, and 6F are the two-dimensional chromatograms for the 25%, 50%, and 75% weathered diesel fuels, respectively. It is evident from the traces that the light hydrocarbon content is gradually reduced as weathering (evaporation) was increased. While the operation and data review of GCxGC-TOFMS may be more complex than typical GC-FID and GC-MS work, the value of such fingerprints to visualize clear differences among the samples is undeniable.

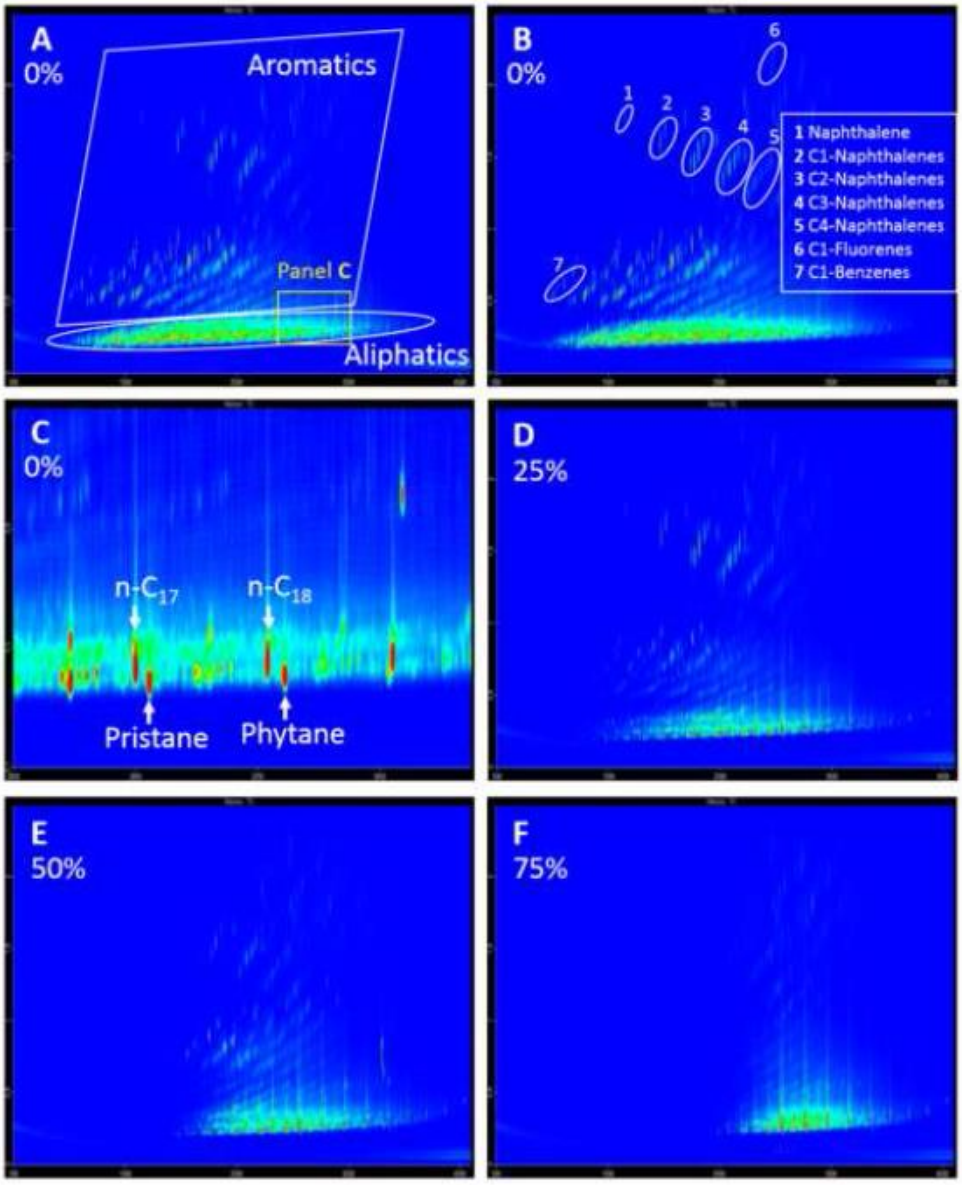

Figure 4-6 GC×GC-TOFMS two-dimensional chromatograms for the separation of unweathered (0%) composite diesel fuel, indicating resolution of (A) general compound classes (the region amplified to obtain panel (C) is shown), (B) different aromatic compound classes, and (C) a region of the chromatogram where high abundant biomarkers can be specified. Further presented are the separation of (D) 25%, (E) 50%, and (F) 75% weathered diesel fuel samples.

4.4.3 Diesel biomarker analysis by GC-VUV and GC×GC-TOFMS.

The isoprenoid molecules pristane and phytane are two petroleum biomarkers that have been well established and widely used in diesel correlation analysis. Ratios of C_{17}/pristane, C_{18}/phytane, and pristane/phytane are determined for age dating analysis. The normal alkanes C_{17} and C_{18} are more susceptible to environment influences (weathering) than pristane and phytane [1,2,12]. Carefully chosen markers can, in general, be used to determine the relative age and the degree of weathering of fuel samples [1]. Meanwhile, comparing the ratios helps reduce dilution effects, and other errors due to the residence of the sample in the environment. Errors that can be introduced from sample preparation and instrumental analysis can also be minimized in this fashion [2].

The weathered diesel fuels and unweathered diesel fuel were analyzed by GC-VUV, GC-FID, and GC×GC-TOFMS to compare measured biomarker ratios. A fuel oil degradation standard, which contained C_{17}, pristane, C_{18}, and phytane, was independently analyzed on the GC-VUV to ensure appropriate assignment of the analyte peaks in the diesel samples.

Normally, one-dimensional GC using FID may be sufficient to define biomarker ratios; however, if the samples are too complex, interferences from coeluting compounds will complicate the analysis. Especially when the sample is more heavily degraded, greater error can be present. For instance, if C_{17} coelutes with a minor compound, which has a very small contribution to the C_{17} peak on GC-FID, then it may be acceptable to use the whole peak area to estimate the biomarker ratio. However, in the case of biodegraded diesel, a larger amount of C17 may be lost relative to pristane. In this case, the relative proportion of the minor coeluting compound may be much higher and more significant. GC-FID would not be able to be used to easily recognize this significant effect and thus an overestimation of the C_{17} peak area might result, skewing subsequent analyses. With GC-VUV, as shown in Figure 4-5, one can first

evaluate the compounds that are coeluting together based on the absorbance of the overall peak, and then deconvolve the peak based on the individual spectrum of the analytes to calculate the exact contribution of the target peak. Thus, a more accurate biomarker ratio could be obtained.

Table 4-1 Comparison of key component ratios for characterization of weathered diesel using different chromatography and detection techniques

		GC x GC TOFMS	GC-FID	GC-VUV
0%	**Pristane / Phytane**	1.360	1.2 ± 0.2	1.15 ± 0.01
	Pristane / C17	0.860	0.47 ± 0.01	0.463 ± 0.005
	Phytane / C18	0.710	0.39 ± 0.03	0.408 ± 0.004
25%	**Pristane / Phytane**	2.280	2.4 ± 0.1	2.3 ± 0.4
	Pristane / C17	0.960	0.89 ± 0.01	0.98 ± 0.04
	Phytane / C18	0.500	0.48 ± 0.01	0.50 ± 0.09
50%	**Pristane / Phytane**	2.260	2.23 ± 0.03	2.47 ± 0.04
	Pristane / C17	1.080	0.790 ± 0.004	0.840 ± 0.005
	Phytane / C18	0.480	0.380 ± 0.002	0.381 ± 0.005
75%	**Pristane / Phytane**	1.360	2.107 ± 0.09	2.54 ± 0.08
	Pristane / C17	0.890	0.777 ± 0.006	0.87 ± 0.05
	Phytane / C18	0.650	0.368 ± 0.008	0.317 ± 0.006

In Table 4-1, the biomarker ratios obtained from both the GC-VUV, GC-FID, and GCxGC-TOFMS analyses are shown. The GC-VUV and FID measurements were performed in triplicate. We can see that the ratios obtained from GC-VUV are closely matching the results from the GC-FID and are characterized

by around 10% variation other than the pristane/phytane ratio, which has also been observed that has a big discrepancy from the results obtained using GC×GC-TOFMS. We can see that either from GC-VUV, GC-FID or GC×GC-TOFMS, the biomarker ratios of 0% and 75% weathered diesel fuel are similar, but different from the ratios of 25% and 50% weathered diesel fuels. It was only discovered after analyzing the diesel samples that the vendor did not link the original source and weathered diesel samples in the sets they manufactured (information provided by Restek). At the same time, this result does exemplify how such an analysis can be used to fingerprint and relate samples of diesel fuel. Even though both the 0% and 50% weathered samples contained biodiesel components (Figures 4-1A and 1C), their origination can be considered different based on the disparity of the measured biomarker ratios. Greater error in measured ratios were found for the 75% weathered diesel fuel. This is likely attributable to the overall reduction of both alkanes and isoprenoids after extensive evaporation. This explains why the ratios from 75% diesel has much higher differences between instruments. From table one we can conclude that GC-VUV was able to achieve the performance of the traditional 1D GC-FID, but the GC-VUV also provides for ability to better classify components. On the other hand, because the VUV library does not contain sufficient spectra for higher chain iso-paraffins and naphthenes, qualification and quantification can still be subject to significant error. However, overall, the GC-VUV results are still quite comparable to those from the other two techniques.

4.5 Conclusion

In this work, GC-VUV has been used to identify different classes of compounds and biomarkers in complex diesel fuel and artificially weathered diesel fuel mixtures. Good agreement was found between biomarker ratios determined by one-dimensional GC-VUV, GC-FID, and GC×GC-TOFMS. While the sample set did not contain specifically related samples, the biomarker ratios along with other details (the presence of fatty acid methyl esters in biodiesel-containing samples) could help differentiate and relate dissimilar and similar samples, respectively.

The VUV is an absorption detector, which may be a simpler concept to convey to a courtroom audience in an environmental forensics case. However, like GC×GC, it is still a relatively new and growing technique. In order to fully understand the information provided by GCxGC, more complex data processing is required. GC x GC requires more specialized analysts to carry out and troubleshoot, extra data treatment would also be needed for a thorough assessment for different cases. Though it provides significant capabilities for analysis of diesel and other fuels, its acceptance in the courtroom might still have some challenges. However, as the design and commercialization of 2D GC is advanced, it will undoubtedly become more accepted in the forensic community. In this work, we meant to introduce an alternative single dimensional tool for the forensic chemists that is an easier and simpler complementary technique to achieve the comprehensive analysis of fuels. It is acknowledged that the VUV detector is in and of itself a less well-established detection technique compared to flame ionization and mass spectrometric detection, but the focus of this work is to demonstrate for the first time its potential usefulness in this application.

GC-VUV spectral filters may be useful in real samples particularly for the speciation of aromatic biomarkers like dimethylnaphthalenes and trimethynaphathalenes, which can be also used as maturity assessment and rock source identification. However, the nature of the environmental sample would be of prime concern. Further work is needed to evaluate the GC-VUV technology in the context of weathered diesel fuels in real environmental samples. Overall, in a court of law, having multiple corroborating evidences can be good, so perhaps using both of these techniques together can be more definitive.

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Chapter 5

Pseudo-Absolute Quantitative Analysis using Gas Chromatography - Vacuum Ultraviolet Spectroscopy – A Tutorial

5.1 Abstract

The vacuum ultraviolet detector (VUV) is a new non-destructive mass sensitive detector for gas chromatography that continuously and rapidly collects full wavelength range absorption between 120 – 240 nm. In addition to conventional methods of quantification (internal and external standard), gas chromatography - vacuum ultraviolet spectroscopy has the potential for pseudo-absolute quantification of analytes based on pre-recorded cross sections (well-defined absorptivity across the 120 - 240 nm wavelength range recorded by the detector) without the need for traditional calibration. The pseudo-absolute method was used in this research to experimentally evaluate the sources of sample loss and gain associated with sample introduction into a typical gas chromatograph. Standard samples of benzene and natural gas were used to assess precision and accuracy for the analysis of liquid and gaseous samples, respectively, based on the amount of analyte loaded on-column. Results indicate that injection volume, split ratio, and sampling times for splitless analysis can all contribute to inaccurate, yet precise sample introduction. For instance, an autosampler can very reproducibly inject a designated volume, but there are significant systematic errors (here, a consistently larger volume than that designated) in the actual volume introduced. The pseudo-absolute quantification capability of the vacuum ultraviolet detector provides a new means for carrying out system performance checks and potentially for solving challenging quantitative analytical problems. For practical purposes, an internal standardized approach to normalize systematic errors can be used to perform quantitative analysis with the pseudo-absolute method.

5.2 Introduction

Quantitative analysis is the branch of chemistry that deals with efforts to determine the amount of a given component in a mixture. It is an essential and fundamental aspect of analytical chemistry. Quantitative methods can be divided into chemical analysis and instrumental analysis [1]. Based on the concentrations of the species that are being measured, substances to be determined can be divided into

major component analysis (>1% w/w), minor component analysis (0.01-1% w/w), trace analysis (10^{-7}% w/w–0.01% w/w), or ultra-trace analysis (<10^{-7}% w/w)) [2, 3].

Classically, since the beginning of modern chemistry in the nineteenth century, gravimetric analysis and volumetric analysis were applied for chemical analysis. Gravimetric analysis can involve the use of an appropriate reagent to combine with an analyte to form a precipitate. Based on the weight of the precipitate, one can calculate the percent of the analyte in the sample. It is a direct quantitative determination of an analyte based on the mass of a solid [4]. Volumetric, or titrimetric analysis, uses titration techniques to determine the volume of a standardized solution of known concentration needed to react with or indicate an analyte for determination of its concentration. These two types of methods are among the few absolute methods that do not rely on calibration with chemical standards. Even though they are also subject to systematic and random forms of error, analyte interferences, and false positives/negatives, once calibrated (or standardized) they can provide more direct or efficient quantification results than many methods that are based on calibration [5].

Early in the twentieth century, instrumental analysis was introduced. Physical properties, such as conductivity, electrode potential, light absorption or emission, mass to charge abundance, and fluorescence were demonstrated to be useful for quantitative analysis [5]. In contrast to quantitative chemical analysis, instrumental analysis relies on a calibration process. The magnitude of an analyte's external signal response, generated by the electronic instrument, is often proportional to the amount or concentration of the substance analyzed. The measurement methods are indirect, and thus, calibration is essential to measure the response generated from a sample composed from a known amount of analyte, prior to determination of the unknown [6]. The calibration procedure helps account for various systematic errors that may be present.

Because the quantity of analytes in a sample can be divided into major, minor, trace, and ultra-trace components, and also because of the different natures of analytes, instrumental methods must be modified, including appropriate sample preparation and sample introduction steps, for effective quantitative analysis. There are several types of quantitative methods commonly used, including area percent, single point external standard, multiple point external standard, single point internal standard, multiple point internal standard, and standard addition methods. Multiple point calibrations are

overwhelmingly preferred because the range of concentrations or amounts over which the change in instrument response occurs is then predictable.

When the functional relationship between the amount of analyte and macroscopic parameters in a method is established based on physical constants and universal quantities, it can be considered an absolute method, which has superior accuracy and precision relative to methods based on calibration. Gravimetric analysis and volumetric analysis can be considered absolute methods because their efficiency can be theoretically predicted [7]. The analytical signal measured using instrumental analysis depends on many conditions, such as the properties of the analyte, the instrumental parameters, the experimental design, and the presence of accompanying substances (the matrix). Thus, instrumental analysis does not generally involve absolute determinations. The instrumental parameters and experimental conditions can be very complex, which makes empirical calibration necessary. Here, we present a new “pseudo-absolute” instrumental quantitative method that is not based on calibration, but is rather based on an analyte’s physical properties, namely its vacuum ultraviolet (VUV) absorption cross-section.

Gas chromatography vacuum ultraviolet spectroscopy (GC-VUV), which simultaneously collects full spectra (120 – 240 nm) VUV and UV absorption spectra of eluting analytes with up to 100 Hz sampling rate, was recently introduced [8-12]. The VUV detector was demonstrated to have very unique and promising features for a wide range of applications. It has the ability to differentiate isomers, where mass spectrometry (MS) has difficulties, and it also is able to deconvolute co-eluting peaks based on known absorbance spectra for different analytes [8, 9]. The analysis of complex mixtures of permanent gases consisting of low molecular weight hydrocarbons, inert gases, and toxic species, for instance, from natural gas components and lithium ion battery off-gassing was addressed using GC-VUV [9]. Multiclass pesticide and fatty acid analysis has also been demonstrated; rich gas phase absorption features are exhibited across various chemical compound classes [10, 11]. Pesticide and fatty acid (e.g. cis-/trans-) isomers were easily differentiated, which indicated that the VUV detector is a good candidate for enhanced speciation relative to MS. Additionally, based on the concept that different classes of chemical compounds have different response in various wavelength ranges, spectral filters can be designed and implemented pre- and post-run to help distinguish families of compounds in a complex mixture.

In addition to conventional quantification methods, GC-VUV can also quantify based on a known cross section for a molecule. It is an absorption spectroscopic method that can be applied to directly determine the amount of substance present in the flow cell. In this wavelength range, the energy of photons are coincident with the energy necessary to excite ground state electrons in molecules. The term cross section indicates the wavelength-dependent absorptivity coefficient in gas phase absorption, which is similar to absorptivity (or molar absorptivity) as in the Beer-Lambert Law. Measured absorbance can be integrated either over full or partial wavelength regions after the full-range absorbance spectra was recorded. The chromatogram is then integrated to determine a peak area. The peak area depends on several different factors: The amount of analyte that passes through the detector; the cross section for the analyte over the wavelength region; the total flow rate through the cell (GC and make-up); and the cell geometry (cell volume and light-path length). When the analyte cross section is known, all of these quantities are known except for the amount of analyte. The measured peak area is used to solve directly for the unknown amount of analyte that passes through the detector. The VUV library contains a large amount of analyte reference spectra that are obtained from prepared standards. The cross section per molecule for analytes can be determined by correlating a reference spectrum with a specific amount of the analyte through the use of a scaling factor. This methodology is derived from Beer-Lambert law and considered to be pseudo-absolute in nature [7], because the conversion of the detector-determined amount to that which was in the sample relies much on contributions from the efficiency of sample preparation, sample introduction, and any other processes that may occur before the analyte reaches the detector.

Sampling, sample treatment, sample introduction, separation parameters, detector settings, and appropriate replication are all important considerations to produce a reliable quantitative study. Error cannot be avoided and must be carefully accounted. Pseudo-absolute quantification can be used to systematically locate errors and inaccuracies, so they can be corrected, if necessary. In gas chromatography, several specific processes can be assessed. Injection is an integral part of sample introduction and choosing the wrong syringe can create significant errors. Different injection techniques and syringe sizes should be considered depending on the application. The injection port liner also serves a very important role in GC, as it facilitates rapid and uniform vaporization and transfer of the sample onto

the column. The sample injection volume must be such that its vapor cloud does not exceed the liner volume, in order to avoid backflash. Choosing the wrong liner or poor injection volume settings can lead to poor separations, poor peak shape, and/or sample discrimination [13].

The most common inlet for GC is a split/splitless injector. Depending on the application, the settings of the injector need to be carefully optimized. For instance, sampling time, the time for which the split vent is closed during a splitless injection, should be adjusted to ensure complete loading of the sample from the liner onto the column. During this time, it is conceivable that the septum purge flow can also be a source of sample loss. For split injections, the split ratio effectively determines the volume fraction of the sample vapor that enters the column. This usually needs to be empirically adjusted to obtain good sensitivity and peak shape [14], but the accuracy of such settings are not well defined. Finally, hardware connections can be a source of error. Poorly tightened or over tightened column connections can cause sample losses. If errors from such settings can be diagnosed and addressed, then instrument performance will be significantly enhanced. Other than these errors, there are of course some other potential errors that also could be introduced from, for instance, the types of pipets used and volumetric flasks. Some solvents are very volatile, which could lead to a higher concentration of analytes than expected if the sample vial is not well sealed or held for an extended period. As is standard for such research, these variables need to be carefully controlled using proper equipment and best practices in sample preparation and handling.

The primary aim of this study was to demonstrate pseudo-absolute quantification using a VUV detector to investigate instrumental parameters and associated systematic errors that may be encountered in gas chromatography sample introduction. The VUV detector was used to perform absolute quantification of systematic errors. Benzene and natural gas were used to assess error or sample loss/gain for the analysis of liquid and gaseous samples, respectively. Injection volumes, syringe sizes, inlet port variables for split and splitless injections, and column connections were studied to determine their impact on sample losses. While a calibration model can account for consistent and reproducible losses, absolute settings of instrument parameters were found to contribute, in some cases unexpectedly, to sample gain and loss, as determined by pseudo-absolute quantification. A comparison of results obtained from standard calibration using benzene was made with that obtained by the pseudo-

absolute method. In cases where variables could be controlled and corrected, correlating the amount of analyte in the detector cell with the amount introduced is feasible. For practical purposes, the use of an internal standard can be considered to normalize sample losses. The results provide renewed insight into the details of hardware settings for GC analysis. The VUV detector can be an effective diagnostic, but it also provides means for considering calibrationless analysis in future applications.

5.3 Experimental

5.3.1 Instrumentation

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia MD), equipped with a AOC-20i auto injector, was coupled to a VGA-100 VUV detector (VUV Analytics, Inc., CedarPark TX). The column used for both benzene and natural gas analysis was a Rt®-Q-BOND (30 m × 0.32 mm × 10 µm) from Restek Corporation (Bellefonte, PA). The instrument was operated in the constant velocity mode (27 cm s^{-1}) with helium carrier gas. The syringes used for benzene sample introduction were 10 µL and 0.5 µL syringes from SGE Analytical Science (Austin, TX). For natural gas introduction, a 1 mL Pressure-Lok VICI gas tight syringe from SGE Analytical Science was used. A Sky® 3.5 mm ID single taper inlet liner with glass wool from Restek was used for all the applications. Nitrogen was used as a post-column make-up gas and was set to 0.25 psi. The flow meter applied to record the exit port flow rate was a ProFLOW 6000 electronic flowmeter from Restek Corporation. The column oven programs for the benzene and natural gas analyses were identical, for the sake of consistency throughout the experiments. The oven was set to start at 50 ◦C (held for 4 min) and then increased to 200 ◦C at a rate of 15 ◦C/min (held for 10 min). The injection port temperature was set to 250 ◦C. The injection volume and split ratio were varied depending on the experiment. The detector spectral acquisition rate was set at 2.7 Hz. The transfer line and flow cell temperatures were set to 300 ◦C.

5.3.2 Sample Preparation

A 150 ng/µL benzene sample was prepared in dichloromethane as a solvent. Benzene was purchased from Sigma-Aldrich (Milwaukee, WI) and dichloromethane was from EMD Millipore Corporation (Billerica, MA). A range of concentrations (0, 25, 50, 100, 150, 200, and 400 ng/µL) of benzene were prepared for calibration to compare results with the pseudo-absolute method. A 100,000 ng/µL toluene solution in dichloromethane was prepared and diluted to 150 ng/µL for use as an internal standard. Toluene was purchased from EMD Millipore Corporation. A natural gas standard containing nitrogen, carbon dioxide, methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, and hexanes was obtained from ISGAS, Inc. (Houston, TX). The composition of the standard is shown in Table 5-1.

Table 5-1 Concentration of different components in a natural gas standard

Components	**Mole Percent by Volume**
Nitrogen	1.001
Carbon Dioxide	0.520
Methane	94.734
Ethane	2.002
Propane	0.754
Iso-butane	0.303
Butane	0.302
Iso-pentane	0.151
n-pentane	0.151
Hexanes+C10 Extended	0.101

5.3.3 Pseudo-absolute quantification theory

GC-VUV has the ability to quantify and identify analytes based on known absorption cross-sections of gas molecules in the VUV regime. The measured absorbance spectra for analytes can be compared to their respective cross sections to verify the analyte composition. Reference spectra based on normalized absorbance (for qualitative analysis) and absorption cross-sections (for both qualitative and quantitative analysis) are recorded in a library that can be accessed through the VGA-100 software. Figure 5-1 shows recorded absorption cross sections of methane, ethane, and benzene.

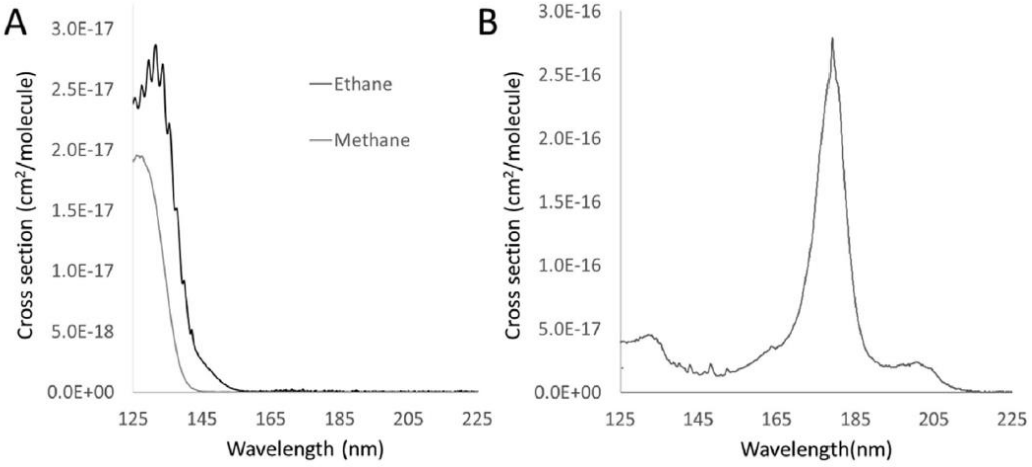


Figure 5 -1 Recorded cross sections for (A) methane, ethane and (B) benzene.

The absorbance for a given amount of analyte (defined for a given wavelength or wavelength range λ) can be described as:

$$A(\lambda) = \frac{1}{\ln(10)}\sigma(\lambda)\frac{N}{V}d \qquad (1)$$

where σ is absorption cross section (cm^2/molecule), and is similar to ε (or a, absorptivity) in the well-known Beer-Lambert Law, which indicates the wavelength-dependent absorptivity coefficient. N is the number of analyte molecules, V is the sample cell volume, and d is the light-path length. During a chromatographic measurement, each absorbance scan is integrated over a wavelength interval. "Integration" refers to an operation used to convert an absorbance spectrum to a single-valued chromatographic response. Any number of integration schemes can be employed for this purpose, as long as the same procedure is applied to absorbance and cross section spectra. In this work, the chromatographic responses were generated by averaging the absorbance and cross section spectra over

a given wavelength region of 170-200 nm and 125-160 nm for benzene and natural gas component (methane and ethane) quantification, respectively.

The integrated absorbance increases from baseline through a maximum and back to baseline as the analyte molecules pass through the flow cell, forming a chromatographic peak. A peak area (PA) can be determined via numerical integration of the chromatographic response over the time region of a peak. In terms of quantities of interest, such as the amount of analyte on-column, the peak area can be expressed as:

$$PA = \frac{1}{\ln(10)} \frac{d}{F} \Sigma N_{col} \qquad (2)$$

where N_{col} is the total number of analyte molecules introduced on column and F is the sample cell flow rate. Σ is the absorption cross section integrated over the same wavelength region as the absorbance. After measuring the peak area, PA, and providing the cell length, flow rate, and integrated cross section, Equation 2 can be solved to find the total number of on-column molecules, which can then be used to determine the on-column mass.

Since additional information about the sample introduction are provided, such as injection volume and split ratio, the measured amount of analyte can be converted to a volume concentration (ppmv):

$$ppmv = \frac{10^6 m(SR+1)}{\rho V_{inj}} \qquad (3)$$

where m is the total on-column analyte mass, SR is the portion of the sample that exits the split vent, and V_{inj} is the volume of injected sample. ρ is the analyte density at sample temperature and pressure, where either the liquid- or gas-phase density is used depending on whether liquid or gaseous samples are introduced to the GC-VUV system. Sample mass/mass or mass/volume concentrations can also be determined via suitable modification of Equation 3.

For the purposes of this work, the peak area was not determined by strict numerical integration, but was instead determined by simply summing the integrated absorbances over a chromatographic peak. This can be done as long as Equation 2 is modified to account for the detector scan rate:

$$PA = \frac{1}{\ln(10)} R \frac{d}{F} \Sigma N_{col} \qquad (4)$$

where R is the detector scan rate, usually expressed in scans/minute or scans/second depending on the units used for flow rate, and the peak “area” PA is actually just a sum of chromatographic scans over the time region of the peak. In most cases, a background contribution was sampled nearby a peak and that contribution was subtracted out of each scan before the sum was performed.

5.4 Results and Discussion

5.4.1 System diagnostics for liquid sample injection

The various settings specified for GC sample introduction can be a source of error for quantitative analysis. While these can typically be calibrated, their presence will significantly impact the accuracy of a pseudo-absolute quantification result. With the absolute detection capabilities of the detector, it is possible to diagnose the magnitude of impact of each parameter. It would then possible to devise a correction for systematic error in each to make a pseudo-absolute quantification result more meaningful for the determination of an analyte in the introduced sample. From a more practical stance, diagnostic procedures to ensure proper day-to-day instrument operation is a best practice that can be facilitated by this technique. The error associated with the following factors was assessed: Splitless sampling time (sometimes called “hold time”); septum purge flow rate; syringe volume; injection volume; split ratio; and column connections.

5.4.1.1 Sampling time diagnostic

Controlling and optimizing the sampling time by actuating the split valve to purge the inlet at some point after injection is the principle in splitless injections. The split vent is kept closed for enough time to allow transfer of the maximum amount of sample vapor on column. After this time, the split vent is opened to sweep the injection port. Too short of a sampling time will unintentionally discard some of the sample before it is loaded on column, which lowers sensitivity. On the contrary, too long of a sampling time can lead to peak fronting, especially for solvent peaks, and a rising baseline[14]. These effects may be mitigated by solvent focusing, i.e. where the initial oven temperature is set 10 – 20 ^{o}C below the boiling point of the solvent, by use of a retention gap (a length of uncoated deactivated fused silica ahead of the

analytical column), or by stationary phase focusing (a thick film of strongly retentive phase that focuses the band at the head of the column).

Different splitless sampling times were tested (0.25, 0.5, 1.0 and 1.5 min) for a 0.2 µL injection (10 µL syringe) of a 150 ng/µL solution of benzene in dichloromethane to determine the optimal sampling time using a 1 mL/min septum purge flow rate. A theoretical mass of 30 ng should be expected, if all of the benzene was effectively loaded. As shown in Figure 5-2A, a short sampling time results in incomplete analyte transfer to the column. Residual vaporized benzene in the injection port is swept free of the system when the split vent is opened too early. Figure 5-2A also shows the calculated mass of benzene and the efficiency based on the pseudo-absolute method. The peak area based on the VUV absorption measurement and the cross-section of benzene (among other factors denoted in Equation 4) was converted to an amount of analyte registered in the detector. When compared to the theoretical amount injected, the efficiency of benzene detected varied from 49 – 111% when the sample time was varied between 0.25 and 1.5 min. Maximum efficiency was obtained with a sampling time above 0.5 min; Sampling times of 1.0 and 1.5 min provided maximum and essentially equivalent efficiency.

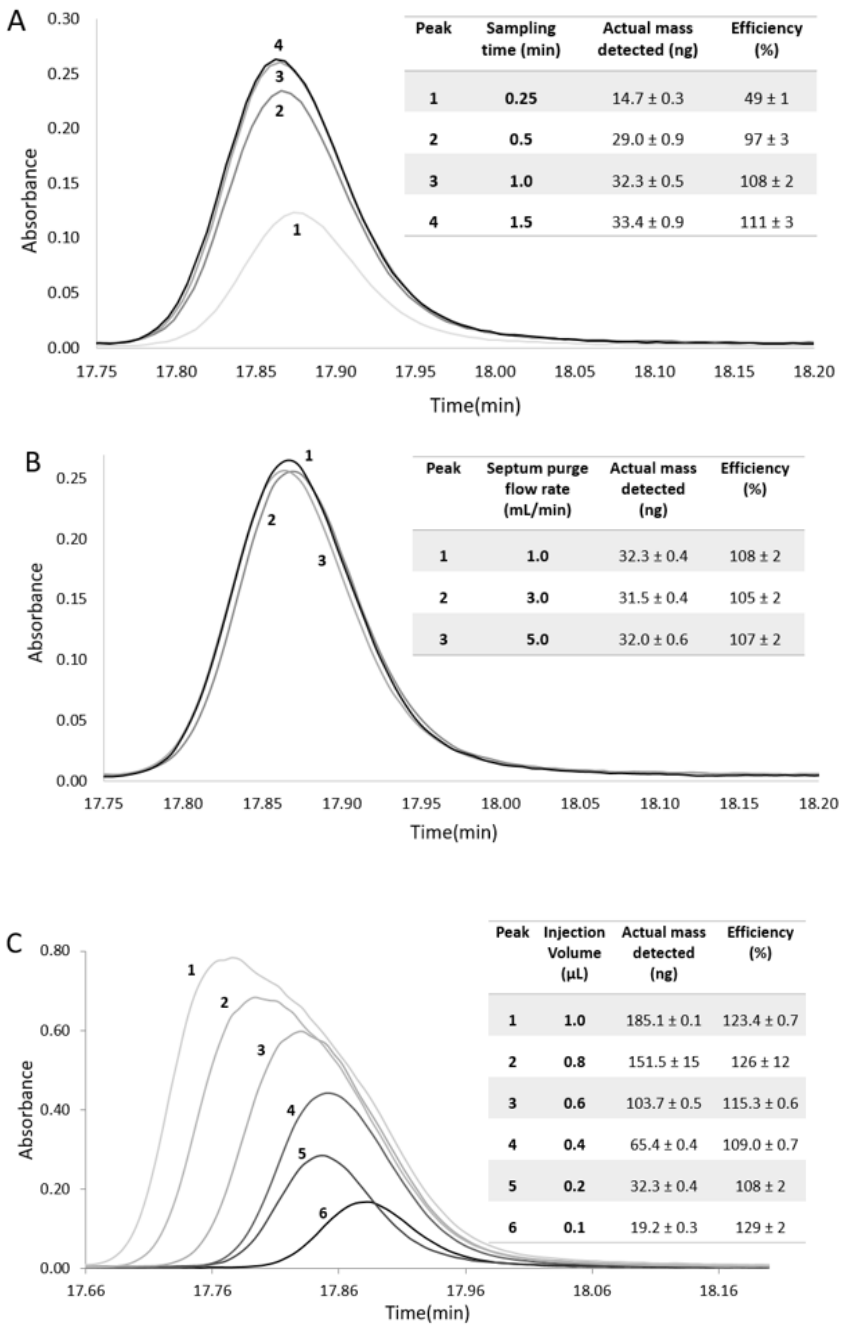
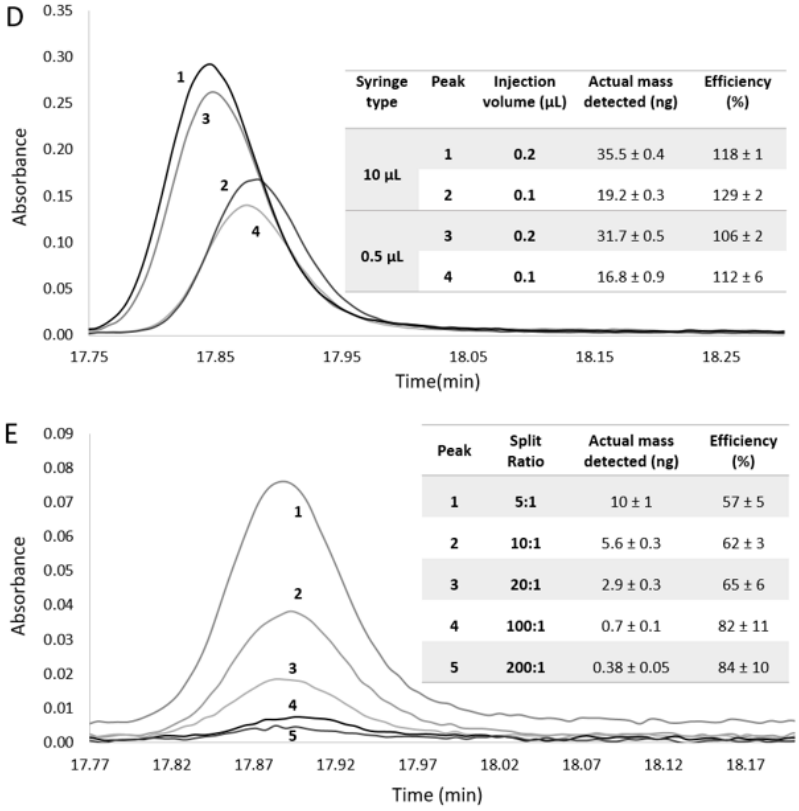


Figure 5-2 Average (n = 3 runs per condition) GC-VUV chromatograms and quantification results for the analysis of 150 ng/µL benzene sample using split and splitless injection modes with different settings: A) Sampling times (0.25, 0.5, 1.0, and 1.5 min) with 1 mL/min septum purge time in splitless mode with expected mass of 30 ng each; B) septum purge flow rates (1.0, 3.0, and 5.0 mL/min) with 1 min sampling time in splitless mode with expected mass of 30 ng each; C) injection volumes (0.1, 0.4,

0.6, 0.8, and 1.0 µL) using a 10 µL syringe in splitless mode with expected mass of 15, 30, 60, 90, 125, and 150 ng respectively; D) different injection volumes (0.1 and 0.2 µL) with different size syringes (0.5 and 10 µL capacity) with expected mass of 15 ng for 0.1 µL injection and 30 ng for 0.2 µL injection; and E) split ratios (5:1, 10:1, 20:1, 100:1, and 200:1) with expected mass of 18, 9, 4.5, 0.9, and 0.45 ng respectively.



Syringe type	Peak	Injection volume (µL)	Actual mass detected (ng)	Efficiency (%)
10 µL	1	0.2	35.5 ± 0.4	118 ± 1
	2	0.1	19.2 ± 0.3	129 ± 2
0.5 µL	3	0.2	31.7 ± 0.5	106 ± 2
	4	0.1	16.8 ± 0.9	112 ± 6

Peak	Split Ratio	Actual mass detected (ng)	Efficiency (%)
1	5:1	10 ± 1	57 ± 5
2	10:1	5.6 ± 0.3	62 ± 3
3	20:1	2.9 ± 0.3	65 ± 6
4	100:1	0.7 ± 0.1	82 ± 11
5	200:1	0.38 ± 0.05	84 ± 10

Figure 5-2 (Continued).

5.4.1.2 Septum purge flow rate diagnostic

In order to reduce the number of contaminant compounds reaching the GC column or the detector, the septum is continuously purged from the underside at a set flow rate [15]. This protects the GC system from sample carryover and compounds released by the heated septum, which improves both qualitative and quantitative analysis [14]. Different septum purge flow rates were tested (1.0, 3.0, and 5.0 mL/min) in conjunction with a 0.2 µL injection volume (10 µL syringe) in splitless mode with a 1 min

sampling time to determine the effect of the rate of the purge on sample loss. It was conjectured that a high septum purge rate during splitless injection could cause an avenue for sample loss.

The same benzene sample as used previously was injected, thus imparting a theoretical mass on-column of 30 ng (assuming no loss). Figure 5-2B depicts the results of triplicate injections of the sample using the different septum purge flow rates. The different septum flow rates had essentially no effect on sample loss. The results in the tale in Figure 5-2B confirm the negligible impact of the three different septum purge flow rates tested, which means that reducing or increasing this flow does not necessarily increase or decrease the efficiency relative to expected theoretical mass transferred to the column. This can be explained by the engineering of the injection port. The directionality and flow rate of carrier gas through the liner is sufficient to direct the majority of the sample onto the column. Additionally, the injection volume used did not come close to overloading the liner, and thus, sample vapor never encountered the septum purge. It makes sense that the injection port would be designed to ensure that there is minimal influence of the septum purge rate on column loading during splitless injections.

5.4.1.3 Injection volume diagnostic

The accuracy and reproducibility of quantitative analysis, and the chromatographic peak shape, can be substantially affected by the amount of sample injected. If the total volume of the sample after vaporization in the inlet is greater than the inlet liner volume, backflash occurs. The injection port becomes overloaded and sample vapor enters the inlet gas supply and septum purge lines where the temperature is significantly lower. The sample vapor recondenses and accumulates on the wall of the gas lines and is reintroduced into the column as a second, broader peak. Excessive carry-over will compromise the accuracy and skew measured values higher, potentially leading to false positives [14]. This is one reason why it is essential to regularly analyze blank samples during analysis batches, to assess for the presence of carry-over, especially when injection volume is maximized to a point where it produces a vapor volume close to the maximum capacity of the liner. The liner volume in the GC inlet port was 457 µL. Since dichloromethane does not have a high thermal expansion upon vaporization, liquid injection volumes ranging from 0.1 – 4 µL, which correspond to vapor volumes of 9.8 – 390 µL, will

not overload the injector [16]. Dichloromethane is thus a good solvent to choose for larger volume injections, when sensitivity needs to be maximized.

A series of different injection volumes (0.1, 0.4, 0.6, 0.8, and 1µL) in splitless injection mode was performed with a 10 µL syringe to determine their effects on measured sample efficiency with 1 min sampling time and 1 mL/min septum purge flow rate. Using the 150 ng/µL benzene standard, the theoretical mass loaded detected ranged from 15 to 150 ng. Figure 5-2C shows average triplicate data for each of these injection volumes. At a 0.4 µL injection volume, the symmetry of the benzene peak began to deteriorate. Column overload is evident due to the extreme fronting observed as injection volume was increased.

Based on the results, we can see that all of the efficiencies are higher than 100%. There appears to be a systematic error in the injection volume applied. Many of the previous analyses described also showed efficiencies higher than 100%. For example, if the system is set to inject 0.2 µL, it can do so reproducibly, but the data indicate that a volume greater than 0.2 µL was actually introduced. A correction curve (Figure 5-3A) was produced to visualize how much systematic error was introduced with different injection volumes. The relative error at each setting stays reasonably consistent across the different volume settings. Knowing the actual amount of analyte registered in the detector through its absolute determination, it is possible to back calculate the additional volume introduced with different injection volume settings. Such error curves are commonly created to correct errors in volumetric glassware, but without the VUV detector or some other absolute detection technique, it would be very difficult to determine such errors in GC sample introduction. It is worthy to note that after injecting 2, 3, and 4 µL volumes of our benzene in dichloromethane, we tested blanks, and no carry-over of benzene (evidence for overload of the inlet liner) was observed, as expected (data not shown).

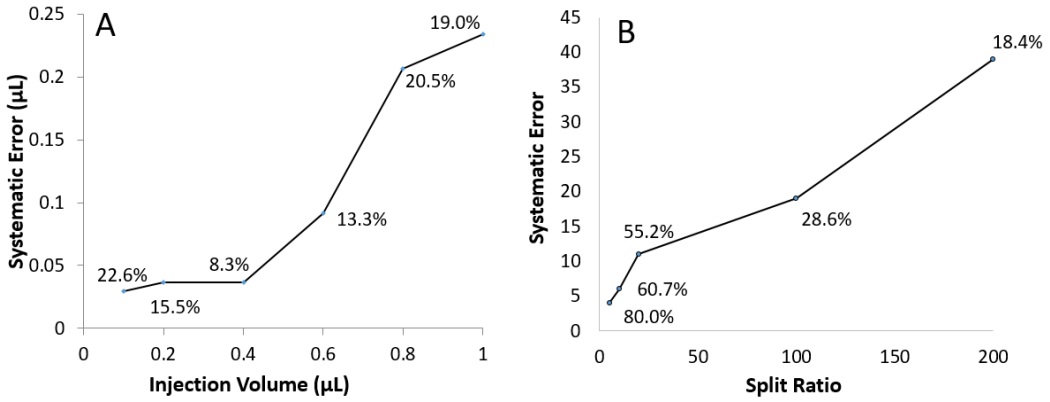


Figure 5- 3 Correction curves for systematic errors and relative errors (next to data points) associated with A) injection volumes (splitless injection mode) using a 1 min sampling time and B) split ratios, both using a 10 µL syringe.

Practically speaking, it may not be desirable to create correction curves for all GC inlet parameters in order to enable direct pseudo-absolute determinations. These corrections would be needed if one was to back calculate the amount of analyte in the original sample relative to what was registered in the detector. That said, as a diagnostic, the ability to assess these errors is useful. From day to day, it could be a simple matter to ensure that the instrument is not subject to any changes in performance. This could be quite useful where repeated and exceedingly accurate high throughput determinations are emphasized.

5.4.1.4 Syringe volume diagnostic

The most general and often used syringe (provided by the manufacturer to outfit our system) is a 10 µL plunger-in-barrel type syringe, which has a 0.7 µL needle volume. This 10 µL syringe is specified to accurately inject liquid volumes ranging from 1.0 – 10 µL. As it is common to inject less than 1 µL in GC experiments, it could be expected that, while a large volume syringe could precisely repeat an injection volume less than 1 µL, the accuracy of such an injection might suffer. When one calibrates under a defined set of instrument settings (including injection volume), minor inaccuracies may not be a problem. However, when using the VUV detector to make an absolute determination of the amount delivered on

column, deviations from the desired injection volume become apparent. An alternative means to obtain more accurate low volume injections is to use a smaller capacity syringe (e.g. 0.5 µL) [17].

We briefly compared the results obtained from injections with two different syringe sizes, 10 µL and 0.5 µL. Figure 5-2D shows chromatograms of the benzene sample obtained by injection of 0.1 and 0.2 µL with each syringe. For each injection volume, the amount of analyte loaded onto the column was shown to be slightly less with the 0.5 µL syringe. It is shown that, based on the calculated mass and the efficiency of benzene with different injection volumes using the different syringes, the 0.5 µL syringe was indeed more accurate. Both syringes provided suitable precision, but both still exhibited a positive systematic error. This was likely due to inaccuracies in injection volume metering by the autosampler or too long residence time of the syringe needle in the hot injector port.

These discrepancies would not be an issue if general calibration procedures were followed. However, the manufacturer supplies the autosampler with a 10 µL syringe as the default. If one wants more accurate injection volumes, especially below 1 µL, which are common for GC analyses, then smaller volume syringes should be used. As demonstrated previously for the 10 µL syringe in splitless mode, a correction curve could be generated for any syringe used, in order to account for discrepancies that are introduced during pseudo-absolute quantification. Or, as discussed below, an internal standard approach can be used to compensate for these inaccuracies.

5.4.1.5 Split ratio diagnostic

The splitless injection technique is generally used for trace or ultra-trace analysis [15]. Capillary columns inherently have lower capacity, and as was shown, a splitless injection with relatively high injection volume will deleteriously affect peak shape and, consequently, resolution. Split injections are more common, as the split ratio can be varied to provide optimal column loading, while maintaining sufficient sensitivity to monitor the analyte over a determined range of concentrations. We tested the accuracy of different split ratios (5:1, 10:1, 20:1, 100:1, and 200:1) using a 0.6 µL injection volume of the benzene standard with 10 µL syringe. Figure 5-2E shows the average response of chromatograms for triplicate injection at each split ratio. As expected, the peak area gradually decreased as the split ratio

was increased. While these data were reproducible, it is interesting to understand the accuracy of the split ratio designated by the instrument.

From the table in Figure 5-2E, we can see that when comparing the expected amount of analyte detected with the actual amount, accuracy was quite poor. The expected amount of benzene deposited on-column varied from 18 ng (5:1 split) to 0.45 ng (200:1 split). The efficiency increased as the split ratio was increased up to 200:1. Even so, at 100:1 and 200:1 split ratios, only approximately 80 – 85% of the expected on-column sample load was achieved. When the split ratio was decreased by an order of magnitude, the efficiency became worse (60 – 65%). It is not unexpected that the splitting process would lead to some systematic error [18]. Such settings (including e.g., injection volume, as discussed below) are designed by the manufacturer to be reproducible above all else. In Figure 5-3B is shown a relative error based on this analysis. A significantly greater split ratio than the set value, with the error increasing at higher split ratios, was found for each setting. Variations from exact split ratio settings, as long as they were close to the intended value, would be accounted in standard calibration procedures. For a direct calibrationless determination, which could be facilitated by the use of a pseudo-absolute VUV method, it would be necessary to determine the absolute deviation present or provide other means for its normalization.

5.4.1.6 Column installation diagnostic

Improper installation of columns, specifically in making connections to the injector and detector is another common problem in GC. If connections are overtightened or are too loose, then leaks can be present. The potential for absolute quantification of on-column mass makes diagnosis of such problems realistic. Checking efficiency based on the injection of a known standard following column installation is a simple best practice, which is enabled with the use of the VUV detector. We performed a simple experiment where we intentionally under-tightened the column connection to the injector. On a subsequent injection, we observed a 10% reduction in benzene efficiency (data not shown). We also over-tightened the column, resulting in a situation where the ferrule was deformed and became lodged in the connection piece. While we did not make an injection under this condition, when we extracted the

ferrule and re-connected the column properly, we were able to verify that the system was returned to original operating conditions.

5.4.2 Pseudo-absolute determination compared to traditional calibration

Typical internal and external calibration procedures account for systematic errors in instrumental settings. As long as the values of such settings can be reproduced, a reliable calibration procedure can be performed. However, calibration requires the preparation of a set of standard samples, and it takes additional time to collect the data that will ultimately relate detector responses to prepared concentrations or amounts of standards. As an exercise, we prepared external and internal standard calibrations for benzene (with toluene as internal standard) and compared the results obtained with those determined based on pseudo-absolute quantification. For each calibration level, a separate determination could be made to relate expected versus actual amount of benzene loaded on column. While this pseudo-absolute method is mainly based on physical fundamentals, in order to create reliable pseudo-absolute methods of analysis, a comparison of the accuracy of a pseudo-absolute method with a method based on empirical calibration should be made. In his work describing absolute and pseudo-absolute determination methods, Hulanicki recommends such a comparison to ensure that similar results are obtained [7].

A seven-point calibration was prepared, with benzene concentration levels ranging from 0 to 400 ng/µL. Based on instrumental injection port inlet settings, the theoretical benzene mass injected was 0, 5, 10, 20, 30, 40, and 80 ng, for each calibration level, respectively. The injection volume was 0.2 µL with the 10 µL syringe under splitless injection mode with 1 min sampling time and 1 mL/min purge time flow rate. When we used solely the cross-section of benzene to convert the measured absorption in mass of benzene registered into the detector, the actual mass was measured to be 0, 6, 12, 22, 32, 42, and 87 ng, respectively (Table 5-2). This is shown graphically in Figure 5-4. It can be seen from the figure that the line of actual mass detected series is slightly higher than the theoretical mass, which was determined using the benzene cross-section to calculate the peak area expected if exactly the expected mass detected had been delivered. This result was consistent with the positive systematic errors for sample introduction parameters revealed previously.

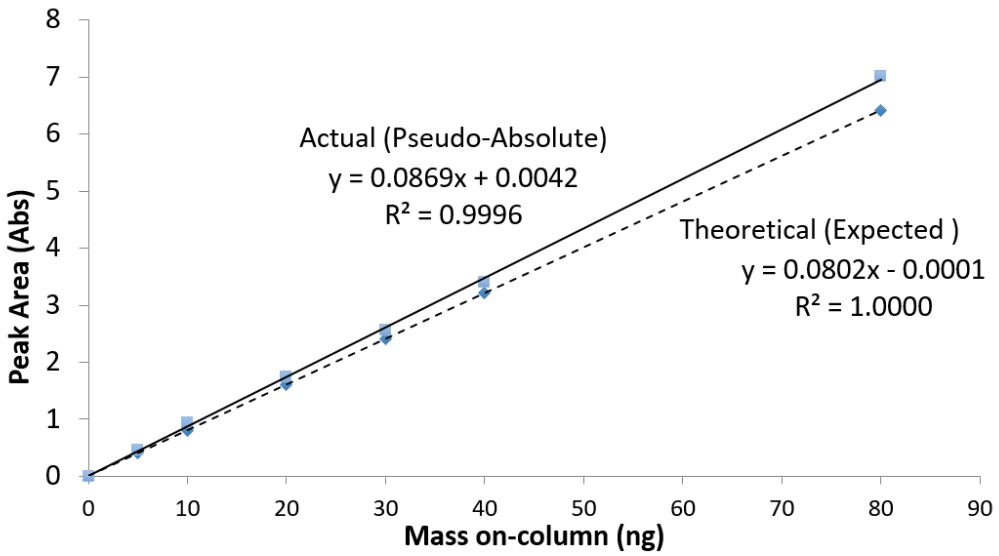


Figure 5-4 Comparison of theoretical benzene mass detected with actual benzene mass calculated based on the pseudo-absolute method through a typical external standard calibration procedure. The injection volume was 0.2 µL under splitless injection mode with 1 min sampling time and 1 mL/min purge time flow rate, using a 10 µL syringe.

An internal standard-based pseudo-absolute approach was also evaluated. As an internal standard, 150 ng/µL of toluene was added to each of the calibration sample vials used to construct the external standard curve shown in Figure 5-4. In this case, if the molecular weight and cross sections of the analyte and internal standard are known and the concentration of the internal standard is known, then the concentration of the analyte can be easily calculated based on the relative peak areas. In this way, systematic errors are normalized and the only uncertainty is that associated with the recorded cross sections, according to the following equation:

$$\frac{PA_2}{PA_1} = \frac{\Sigma_{av,2} N_{col,2}}{\Sigma_{av,1} N_{col,1}} = \frac{\Sigma_{av,2} C_2 \times M_{W,1}}{\Sigma_{av,1} C_1 \times M_{W,2}} \qquad (5)$$

where the peak areas (PA), cross sections (Σ), molecules on column (N_{col}), concentrations (C, in mass/vol), and molecular weights (M_W) are defined for the internal standard (subscript 1) and the analyte (subscript 2). Equation 5 can be derived from Equation 2 applied to both analyte and internal standard, and assumes that the flow rate is the same when measuring PA_1 and PA_2. Equation 5 can then be

advantageously used without needing a separate determination of flow rate, eliminating another possible source of error. If the flow rate is different, it no longer cancels out of the ratio, and Equation 5 can be modified accordingly.

Table 5-2 Preparation and results of the external- and internal standard-based pseudo-absolute determination of benzene at different concentration levels. Toluene at 150 ng/μL is the internal standard (IS).

Prepared benzene concentration	**0 ng/μL**	**25 ng/μL**	**50 ng/μL**	**100 ng/μL**	**150 ng/μL**	**200 ng/μL**	**400 ng/μL**
Expected Benzene detected(ng)	0	5	10	20	30	40	80
Expected IS detected(ng)	30	30	30	30	30	30	30
Benzene peak area (au)	0.02 ± 0.04	0.458 ± 0.006	0.94 ± 0.02	1.73 ± 0.02	2.6 ± 0.1	3.4 ± 0.2	7.0 ± 0.4
Benzene/IS peak area ratio	0.01 ± 0.02	0.207 ± 0.005	0.407 ± 0.005	0.7805 ± 0.0006	1.132 ± 0.005	1.529 ± 0.003	2.97 ± 0.01
Benzene in Detector (ng)	0.2 ± 0.5	5.7 ± 0.1	11.7 ± 0.2	21.6 ± 0.3	32 ± 2	42 ± 2	87 ± 5
Toluene in Detector (ng)	32 ± 2	33.0 ± 0.5	34.0 ± 0.4	33.0 ± 0.5	33 ± 2	33 ± 1	35 ± 2

Determined benzene in sample (ng/µL)	1 ± 2	26.3 ± 0.7	51.8 ± 0.6	99.36 ± 0.07	144.1 ± 0.6	194.6 ± 0.4	378 ± 2

Table 5-2 also shows the calculated benzene mass detected based on using the cross sections of benzene and toluene and Equation 5. The values for the internal standard determination agree well with the values determined for benzene using the pseudo-absolute method directly (denoted Benzene in Detector and plotted in Figure 5-4). Using Equation 4, the amount of toluene internal standard deposited on column can also be determined (denoted as Toluene in Detector in Table 5-2). Consistent with the results for benzene, and based on the systematic errors revealed above, the mass of toluene detected was consistently slightly above the expected 30 ng. The systematic error in the internal standard could then be used to correct for errors in the GC transmission efficiency and to back-calculate a benzene concentration in the sample. These values are much closer to the prepared concentrations of benzene. Though there still existed error in the determined benzene concentrations, systematic error was removed. The results were more consistent with random error, as evidenced by determined values that were both above and below the prepared benzene concentrations.

The internal standard approach can also be used to register cross sections for new compounds of interest. When a known concentration of an analyte for which a cross section is unknown is prepared and introduced into the instrument together with a known amount of internal standard that already has a defined cross section, then the cross section for the analyte can be determined. The internal standard should have similar physicochemical properties as the analyte, so that they are exposed to equivalent systematic errors prior to reaching the detector. For GC analysis, boiling point is one such property to consider.

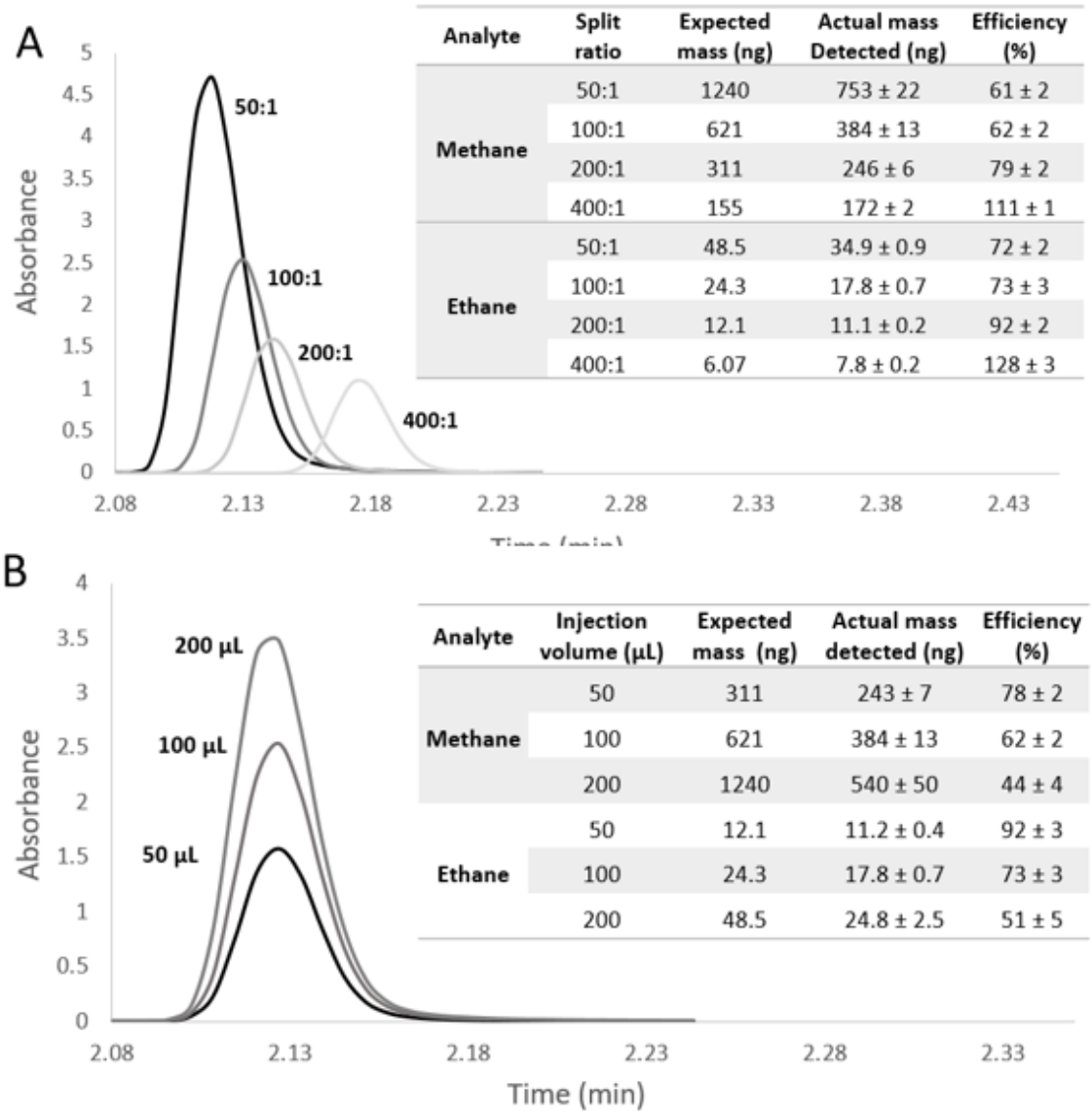
The determination of cross sections is discussed in more detail in a later section.

5.4.3 System diagnostics for introduction of a gaseous sample

The introduction of a gaseous sample into GC is different and more error-prone than liquid sample injection, especially when performed manually. Although a gaseous sample does not require vaporization in a heated injection port, the handling and injection of larger volumes of gases is technically more challenging[19, 20]. Using a natural gas standard sample, we evaluated the potential for systematic errors associated with varying injection volumes and split ratios.

5.4.3.1 Split ratio diagnostic for gaseous samples

Figure 5-5A shows the methane peaks acquired with different split ratios (50:1, 100:1, 200:1, and 400:1) using a 100 µL injection volume. Methane responses observed using the 50:1 and 100:1 split ratio were exceptionally high and saturated the detector. The apex of those chromatograms were modeled and integrated by the VGA-100 software to simulate the original peak areas. This is one potential possibility to introduce error, but it should be a minimal issue because the wavelength dependence of a molecule's gas phase cross-section remains constant and thus, even if the absorption bands around the absorption maximum (~128 nm) are saturated, the overall response can be modeled based on the intensity of the absorption profile at longer wavelengths. As shown in Figure 5-5A, the peak area for methane diminished (49%, 36%, and 30%) with an increase of split ratio, as expected. Shown are the calculated masses of methane and ethane, and the efficiency for each based on the absolute measurement. Less error in the accuracy of the split ratio was observed at higher split ratios. The actual split ratio at 200:1 and lower appears to be higher than the set-point (efficiencies < 80%), whereas at 400:1 it is closer to the expected value or may even be under splitting the sample (> 100% efficiency).



Analyte	Split ratio	Expected mass (ng)	Actual mass Detected (ng)	Efficiency (%)
Methane	50:1	1240	753 ± 22	61 ± 2
	100:1	621	384 ± 13	62 ± 2
	200:1	311	246 ± 6	79 ± 2
	400:1	155	172 ± 2	111 ± 1
Ethane	50:1	48.5	34.9 ± 0.9	72 ± 2
	100:1	24.3	17.8 ± 0.7	73 ± 3
	200:1	12.1	11.1 ± 0.2	92 ± 2
	400:1	6.07	7.8 ± 0.2	128 ± 3

Analyte	Injection volume (µL)	Expected mass (ng)	Actual mass detected (ng)	Efficiency (%)
Methane	50	311	243 ± 7	78 ± 2
	100	621	384 ± 13	62 ± 2
	200	1240	540 ± 50	44 ± 4
Ethane	50	12.1	11.2 ± 0.4	92 ± 3
	100	24.3	17.8 ± 0.7	73 ± 3
	200	48.5	24.8 ± 2.5	51 ± 5

Figure 5-5 Average GC-VUV chromatograms of methane and quantification results of methane and ethane with (A) different split ratios (50:1, 100:1, 200:1) using a 100 µL injection volume and (B) injection volumes (50, 100, and 200 µL) using a 100:1 split ratio and a 10 µL syringe.

Although the condition of the analysis was such that the large response of methane at lower split ratios had to be modeled, this trend is corroborated with a similar analysis of the response and efficiency of ethane, which is approximately 2% as abundant as methane in the natural gas standard. It shows that overall higher efficiency for ethane compared to methane was observed for all split ratios. This could be

an indication of discrimination in the injection port or the saturation of detector against the lighter and significantly more abundant methane.

5.4.3.2 Injection volume diagnostic for gaseous samples

Figure 5B shows methane chromatograms with different injection volumes (50, 100, and 200 µL) using a split ratio of 100:1 and the 10 µL syringe. As in the previous experiment, the methane peaks for the higher injection volumes represent those collected from saturated absorption in the low wavelength portion of the absorption spectra; these chromatograms have all been constructed with the aid of software modeling to simulate the original peak area. From Figure 5B, we can see that as the injection volume increased, the accuracy, the reproducibility, and the efficiency all decreased. However, the absolute efficiency is confounded by the error in the set split ratio. A splitless injection analysis would be necessary to establish the true systematic error associated with different injection volumes. The same analysis for ethane introduction was also performed. The same trends are observed, but the efficiency is much higher. Again, assuming that the systematic error from injection volume is equivalent for both analytes, this difference is likely due to discrimination during flow splitting. The flow splitting effect appears to be less dramatic with lower volume sample introduction, but a more comprehensive study would be needed to fully understand whether the split ratio and injection volume are co-variant, and the extent to which this changes for different analytes. Research does show that lower volume split injections are more ideal for concentrated gaseous samples [21].

5.4.4 Determination of cross sections

In principle, the absolute cross section for an analyte molecule can be determined by measuring a standard of known concentration of the analyte, calculating N_{col} from the concentration, injection volume, and split ratio, and inverting Equation 2 (or Equation 4) to solve for Σ. Then, given a measured

absorbance spectrum for the analyte, A(λ), the cross section at any wavelength value λ can be determined from

$$\sigma(\lambda) = \frac{\Sigma}{A_{int}} A(\lambda), \qquad (6)$$

where A_{int} is chromatographic response corresponding to A(λ). For example, if PA and Σ are averages over 125 – 240 nm, then A_{int} is the analyte's absorbance spectrum averaged over the same wavelength region.

However, this procedure is easily thwarted by the same systematic error mechanisms already discussed. A correction factor would typically have to be determined and used to obtain the true value for N_{col}, as any error in this value is directly propagated to the determination of the cross section magnitude. As was already mentioned, many types of systematic error can be addressed by use of an internal standard methodology like Equation 5. When implemented this way, the concentrations of both analyte and internal standard are known, and the cross section of the internal standard is known. Then Equation 5 can be inverted to solve for the analyte's integrated cross section ($\Sigma_{av,2}$ in Equation 5) and Equation 6 used to determine the cross section throughout the measured wavelength region. Such a procedure can determine accurate cross sections, but requires suitable internal standards whose cross sections are themselves accurately known.

Generally, a GC-VUV experiment may not be the most effective way to determine a cross section from scratch, when nothing is known at all about the cross section's magnitude and an internal standard determination is not practical. A somewhat different configuration consisting of a stand-alone VUV spectrometer, that would remove uncertainties associated with GC sample introduction, might be helpful for this determination. This was impractical for the present work, however.

For the model cases presented here, absolute cross section values available in the literature were used along with GC-VUV measured absorbance spectra to generate cross sections for benzene, toluene, methane, and ethane. To do this, Equation 1 was applied to each model compound with inputs consisting of a measured absorbance spectrum and cross section data selected from a publicly available repository [22]. The GC-VUV light-path length and volume are known, and a regression procedure was used to minimize the sum of squared residuals between measured and calculated absorbance by optimizing the remaining unknown, N. Equation 1 was then inverted to determine σ(λ) throughout the

measured wavelength region. Over time, the values for some of the cross sections have undergone minor refinement through various experiments, such as the internal standard procedure described above, or simply updating the corresponding VUV library reference spectra.

5.5 Conclusion

Gas chromatography is a mainstay in research and routine analysis laboratories. Despite its high prevalence and generally established nature, there are many parameters that must be considered and controlled to ensure proper operation. Quantitative analysis requires particularly rigorous calibration and validation steps to ensure precise and accurate results. The VUV detector is a new tool that offers new capabilities for diagnostic and routine quality tests, including the potential for calibrationless determinations, if the cross section of an analyte is known.

Using the capability of the VUV to make absolute determinations of the number of molecules present in the detector, we have shown how various injection port parameters can introduce systematic error into the absolute mass of analyte delivered on column. These can be characterized and corrected so that the amount of analyte registered into the detector can be related back to the amount of analyte in the injected sample – a so-called pseudo-absolute determination. Of course, to trace this value back to an original sample, the efficiencies of any sample preparation steps would also need to be carefully characterized. From a more practical stand-point, the absolute measurement capabilities of the detector can be a useful tool for system diagnostics, especially following routine maintenance, but even on a day-to-day basis. Calibrationless determinations based on the pseudo-absolute method are best performed in an internal standardized fashion, since system errors will be normalized. This could potentially offer a route to reduce the number of analyses required in a batch for calibration, but of course, rigorous validation of the scope of a method (its linearity, limits of detection, and accuracy/precision at various concentration levels) would still be best practice. In the future, it will be necessary to show more real world applications of the pseudo-absolute method. Comparisons of accuracies and precisions for such applications to those obtained by traditional calibration should be performed. In new pseudo-absolute determinations, the accurate determination of absorption cross-sections will be a key aspect of such work.

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Chapter 6

Complex mixture quantification by gas chromatography without calibration standards using a methanizer in conjunction with flame ionization detection

6.1 Abstract

Identification and quantification of complex carbon-containing mixtures are typically very time-intensive tasks with regards to the calibration process. A gas chromatograph with a flame ionization detector yields strong responses to organic compounds and provides a wide linear range over many orders of magnitude; however, responses for highly functionalized and heteroatom containing compounds can be variable. Here a commercial methanizer unit, placed before the flame ionization detector, was investigated as a means of normalizing response. The methanizer includes two catalytic reaction chambers, which converts all carbon-containing compounds to methane (and other inorganic byproducts). It provides equivalent response factor for all the carbon containing compounds with very high sensitivity. Four groups of different complex mixtures from light hydrocarbon mixtures to terpene and polymer mixtures were analyzed to evaluate the potential for calibration-free quantitation of the new detector arrangement. We have obtained accurate quantification results without time-consuming calibration process. The analysis of equimolar hydrocarbons proved the concept of the accurate uniform carbon response. The quantification of terpene mixture and polymer mixture confirm the ability of the Polyarc for analyzing samples that either have complex physical or structural properties or wide concentration range. In the summary, compare to other detectors, Polyarc provides simple workflow by eliminating the calibration steps to increase the throughput that provides more economic analysis.

6.2 Introduction

The flame ionization detector (FID), due to its sensitivity, linearity, and universal response is one of the most popular gas chromatography (GC) detectors [1]. The FID has contributed to GC development over a period of more than 50 years ago, owing primarily to sensitive response to volatile and semivolatile carbon-containing molecules [2]. It has been widely used in many different areas, including in flavor and

fragrance, pharmaceutical, and petrochemical industries [3, 4]. In GC-FID, nearly all carbon atoms from organic compounds eluted from the column will be combusted, leading eventually to the FID signal-producing formylium ion (CHO^+). The negatively biased collector registers the positive ions and generates an electric current, which is proportional to the abundance of the collected ions [5, 6]. The FID detector has many advantages. Because of its simple concept, it is relatively easy to maintain and inexpensive. In addition, the FID is characterized a very wide linear response range, up to seven orders of magnitude, which enables it to measure organic substances at both low and high levels [2]. Also, due to its low detector response to some certain compounds like fixed gases, nitrogen oxides and etc., some applications require complimentary detectors for compounds beyond the FID specificity or sensitivity [2, 5].

Generally, in FID quantification analysis, peak area percentage method, external calibration method, and internal calibration method have been often used with some limitations when it comes to complex sample mixtures, which makes the calibration limited and time consuming [3, 7]. Additionally, experimentally determined response factor has also been applied for quantifying complex mixtures, which is based on the assumption that the detector response is proportional to the molecular mass of each compound and their response factors are equal to 1. However, for big molecules that does not contain much heteroatoms, it will be an acceptable approach, but for small molecules that contain a larger number of heteroatoms, this method becomes much less reliable [2]. Effective carbon number (ECN) is a concept that has been introduced many years ago wither respect to determining organic compounds possessing different heteroatom functional groups using GC-FID [8]. It is assumed that the properties of a functional group in a complex molecule behave independently and the response factor can therefore be estimated. However, the determination of the response factor frequently relies on the chemical functions of the compounds and experimental conditions, which gives different responses for some compounds. Thus, the results that can be obtained are oftentimes different from what has been expected which would invalidate the prediction. Furthermore, literature is not always available for the large variety of different compounds [2, 3, 7, 8].

In GC-FID, organic compounds with highly functionalized group and heteroatoms containing oxygen, nitrogen, sulfur, or halogens have relatively lower responses compared to hydrocarbons. Among

all the hydrocarbons, methane is literally the end point of the reaction of organic compounds with excessive hydrogen atoms due to its strong carbon-hydrogen bond [2]. Commercial methanizer systems, interfaced with GC-FID instruments, have been introduced to the market previously [9]. However, these have been primarily marketed to enable trace level detection of CO and CO_2, upon their conversion to methane. Recently, a more versatile methanizer system was developed and released by Activated Research Company. The so-called Polyarc® system contains two catalytic microreactors, which converts all organic compounds to methane before they reach the FID detector. In this way, every single carbon atom in a compound is detected as a molecule of methane [10]. The first reaction chamber is utilized for catalytic oxidation where the organic compounds are combusted to CO_2 and the second reaction chamber is utilized for reduction to reduce the CO_2 to CH_4. This setup is directly connected prior to the FID detector. Due to the universal response of methane, the response factor for all the organic compounds are equivalent to unity. Therefore, by applying the following equation (1), the carbon content and concentration can be easily determined without calibration and response factors, simply by incorporating an internal standard (std): [10]

$$RF = 1 = \frac{mol\ C\ /\ area}{mol\ C_{std}\ /\ area_{std}} \Longrightarrow mol\ C = \frac{area * mol\ C_{std}}{area_{std}}$$

(1)

The use of a GC-polyarc/FID instrument has been demonstrated previously to determine highly functionalized molecules, including carbon monoxide, carbon dioxide, formic acid, formaldehyde, and formamide with higher detection response compare to a standard FID detector [11]. It also was able to quantify fuel oxygenates with a very simple fashion and no calibration method was involved [12]. Furthermore, it showed the possibility of accurately quantifying 24 different fatty acid methyl esters in a mixture without calibration, using a single internal standard [13].

The aim of this current work was to evaluate the capability of GC-polyarc/FID on hydrocarbon analysis compare to traditional methods like GC-MS and GC-FID.[14] A series of C7-C40 n-alkanes standard was analyzed and quantified to track measurement efficiency of method settings including different split ratios and injection temperatures. Such of settings that are specified for GC sample

introduction are generally being characterized to contribute to systematic errors for quantitative analysis[15]. Terpene, a mixture that contains a large amount of different groups of organic hydrocarbons with a variety of different isomers that have similar physical and chemical properties, has been analyzed to evaluate the quantification ability of GC-Polarc/FID, which is extremely challenging due to the similarity of some molecules and the wide concentration range [16, 17]. Polyethylene glycols(PEGs) are mixtures of varied lengths of ethylene glycol with the structure commonly expressed as $H-(O-CH_2-CH_2)_n-OH$. It can be widely used in various fields including cosmetic industry, food industry, and pharmaceutical industry [18, 19]. Methods of characterization and quantification of PEGs have been largely developed, for instance, HPLC-UV and MS detection, Size exclusion chromatography, supercritical fluid chromatography, and so on [18, 20]. In this research, PEG200, PEG300, and PEG400 have been analyzed. Furthermore, as has been discussed above, to address the problem of not producing FID signal due to the lacking of the CH^+ that produces CHO^+, Polyarc detector converts all the carbon-containing compounds to methane and provide the uniformed response for all the molecules based on a per-carbon atom basis [11]. This unique feature makes the quantification process faster, easier and more accurate. A mixture of equimolar hydrocarbons from C6-C10 was analyzed here to evaluate the quantitative accuracy of the Polyarc system. The primary goal of this research was to evaluate the quantification ability and accuracy of using a GC-FID equipped with a Polyarc detector and to access the performance of the polyarc as a tool of characterizing and quantitating analytes in complex mixture samples.

6.3 Materials and Methods

6.3.1 Sample analyzed

A mixed standard of linear alkanes (C7-C40) obtained from Sigma Aldrich (#49452-U) at 90 mg/L was used to evaluate measurement efficiency of method settings of split ratio and injection port temperature. C9 in the standard was assigned as the internal standard. C10 was spiked into the sample as a retention time marker.

Four commercial turpentine oil samples were analyzed. They are distilled turpentine (Winsor & Newton, A), pure gum of turpentine for cleaning and removing stains (HUMCO, B), pure turpentine gum for external use only (PhytoLab, C), 100% pure gum of turpentine derived from slash pine tree in South Georgia, USA (Dimond G Forest Products, D). The turpentine samples were diluted by methanol for 10 times and 10mg/ml dodecane from Sigma-Aldrich (Milwaukee, WI) was added into the sample as the internal standard.

Ethylene glycol polymer mixtures (Simga Aldrich) of average 200, 300, and 400 da molecular weight (PEG200, PEG300, PEG400, respectively) were separated in order to quantify individual polymer species. 900 mg/L of each PEG mixture with 100 mg/L n-decane as internal standard (IS) was separated.

Hexane (C6), Cyclohexane (C6), Benzene (C6), Heptane (C7), Cycloheptane (C7), Toluene (C7), Octane (C8), n-Nonane (C9), Decane (C10), Naphthalene (C10), Undecane (C11), Dodecane (C12), 1,6-Dimethylnaphthene (C12) were mixed in methylene chloride as the same number of moles, 1.00 mmol. Benzene, Heptane, Cycloheptane, Octane, Naphthalene, Dodecane, undecane, and 1,6-Dimethylnaphthene were obtained from Sigma-Aldrich, Hexane from EMD Millipore Corporation (Billerica, MA), Cyclohexane and n-Nonane from Alfa Aesar (Haverhill, MA), Toluene from J.T. Baker (Center Valley, PA) and n-Decane from Spectrum (New Brunswick, NJ).

6.3.2 Instrumentation

A Shimadzu GC-2010 Plus gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD) was outfitted with a Polyarc micro-reactor (Activated Research Company, St. Paul, MN), placed before and interfaced with a flame ionization detector. Helium was used as the carrier and FID makeup gas. FID flow settings consisted of 350 mL/min air, 1.5 mL/min hydrogen, and 20 mL/min helium makeup. Hydrogen at 35 std. cm^3 min^{-1} and air at 2.5 std. cm^3 min^{-1} were applied to the reactor and controlled by an electronic mass flow controller (Activated Research Company PA-MFC-A09). The column used for all analyses was a Rxi-5MS (15 m x 0.25 mm x 0.25 µm) from Restek Corporation (Bellefonte, PA). A vacuum ultraviolet (VUV) spectroscopy detector, VGA-100 (VUV Analytics, Inc., Cedar Park, TX) was coupled with another Shimadzu GC-2010 for identification of the analytes. Column used on GC-VUV was

a similar Rtx-5 column from Restek Corp. For the analysis of the hydrocarbon mixture, polymer mixture, and equimolar hydrocarbon mixture, the oven was set to start at 50 °C (held for 2 min) and then increased to 320 °C at a rate of 15 °C/min (held for 6 min). For the terpene analysis, the oven was set to start at 35 °C (held for 1.5 min), increased to 75 °C at a rate of 20 °C/min (held for 1 min), increased to 80 °C at a rate of 0.5 °C/min (held for 0 min), and then increased to 200 °C at a rate of 60 °C/min (held for 4 min). For the polymer analysis, the oven was set to start at 50 °C (held for 2 min) and then increased to 325 °C at a rate of 25 °C/min (held for 2 min). Temperature setpoints throughout the system were 300 °C (inlet), 293 °C (Polyarc), and 325 °C (FID). While the Polyarc temperature setpoint was only 293 °C, the actual temperature was much higher due to the electronic isotherm of the microreactor heaters. The injection port temperature was varied for the hydrocarbon mixture analysis. The split ratio was 50:1 for the terpene mixture and equal mole hydrocarbon mixture analysis, 25:1 for polymer mixture analysis, and varied based on the experiments for the hydrocarbon mixture.

6.4 Results and Discussion

6.4.1 Systematic GC accuracy assessment

Instrumental settings such as split ratio and injection temperature were evaluated for accuracy and efficiency, ultimately leading to an understanding of the cause of the hydrocarbon recovery loss. Parameters assessed were injection split ratio (10:1, 50:1, 100:1, 200:1, 300:1) and injection temperature (225 °C, 250 °C, 275 °C, 300 °C, 325 °C). 6 representative hydrocarbons (C12, C15, C20, C25, C30, C35) were chosen to demonstrate in Figure 6-1 the recovery at respective settings. Figure 6-1-A shows the hydrocarbon recovery calculated with different split ratios at an injection temperature of 300 °C. As it shows in the Figure 6-1-A, each set of split ratios, the recovery is decreased as the molecular weight is increased. The noticeable reduced response is due to the broad range of molecular weights and boiling points. Samples that contain analyte groups with a wide breadth of molecular weights and boiling points have more molecular weight discrimination since only one injection port temperature can be applied with

a traditional split injector [21]. Error bars in Figure 6-1-A indicate that high molecular weight hydrocarbons exhibited poor reproducibility at high split ratios. In addition, the recoveries of the small hydrocarbons, for example C12 in Figure 6-1-A, changes very slightly with the variation of the split ratios. In contrast, C35 has more discrepancy with each recovery point. Due to the high temperature that has been applied for higher boiling point compounds, there is column bleeding happened caused the baseline shifting as it is showing in the chromatogram in the figure, which gives difficulty when integrating peak areas and therefore, it is understandable why the heavier hydrocarbons have poor recovery.

Figure 6-1-B shows the recovery calculated with different injection temperatures at a split ratio of 20:1. The recoveries of hydrocarbon decrease as the molecular weight increases. The concentrations of all the hydrocarbons have been calculated based on Equation 1 in one set of triplicate experiments with no calibration involved.

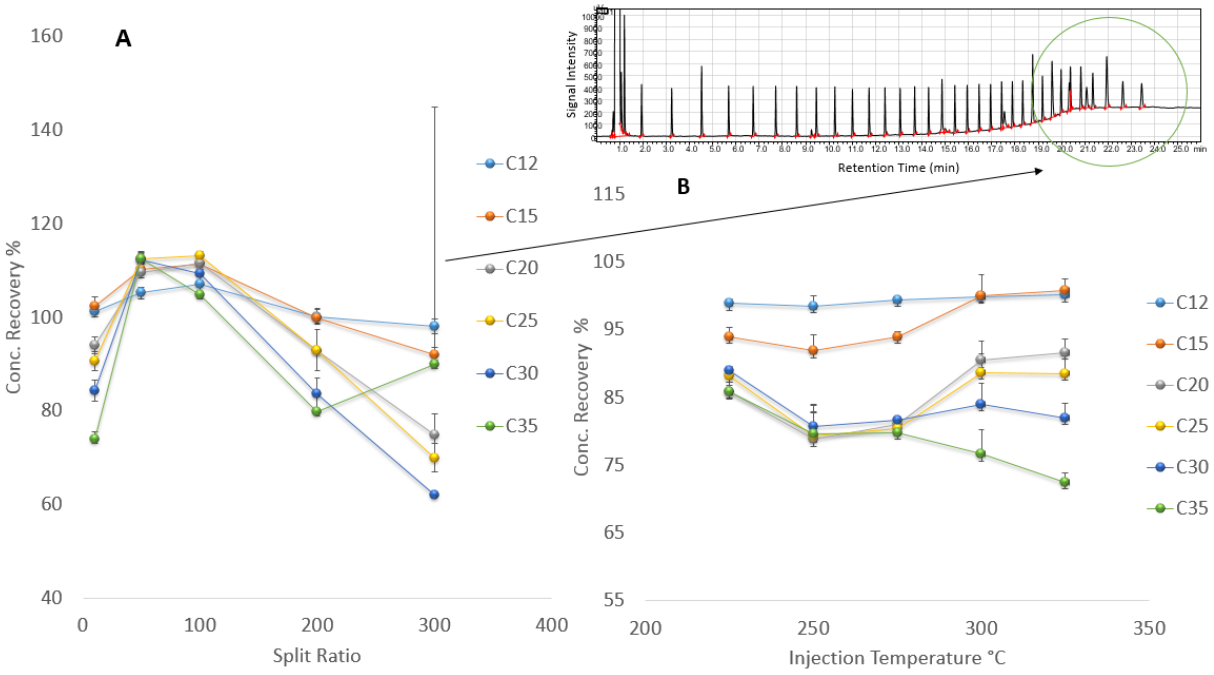

Figure 6-1. Quantification of n-alkanes (C7-C40) with different instrumental settings: A) Split ratios: 10:1, 50:1, 100:1, 200:1, 300:1 with injection temperature 300 °C and 1 µL injection volume. B) Injection temperatures: 225 °C, 250 °C, 275 °C, 300 °C, 325 °C with 20:1 split ratio and 1 µL injection volume.

6.4.2 Quantification of a terpene mixture

Natural mixtures of terpenes have features such as high complexity, similar isobaric structures, and wide concentration ranges that make acquisition of standards and quantification challenging. Turpentine is a flammable, thin essential oil that is obtained from coniferous trees like pine[22, 23]. The major components in turpentine are terpenes, biosynthetic polymers of isoprene, including alpha-pinene, beta-pinene, carene, among many others. Turpentine is applied in various fields, as in the production of chemical solvents, cosmetics, and medical formulations [23]. Due to the great value of turpentine in the industrial application, the characterization and quantification of the components in turpentine oil become more important.

Here, four different turpentine oil samples have been analyzed by GC-Polyarc/FID to assess its ability on complex mixture analysis. According to the product labeling, Turpentine A is distilled turpentine that is used for brush cleaner. Turpentine B is pure gum of turpentine that can be used as solvent or painting oil. Turpentine oil C is pure turpentine gum for external use. Turpentine oil D is a 100% pure gum of turpentine that is derived from slash pine tree in South Georgia, USA. 10mg/ml dodecane was added into each of the sample as the internal standard. Figure 6-2 shows the chromatograms of the four different turpentine oil samples. Chromatograms A, B, C, and D represent samples A, B, C, and D accordingly with almost identical peak population but varying concentrations in some cases. The major peaks that have been detected and quantified are: Alpha-Pinene, Camphene, (-)-beta-Pinene, Beta-Myrcene, p-Mentha-1,5-diene, Delta-3-Carene, d-Limonene, gamma-Terpinene, Terpinolene, Linalool, (R)-Endo-(+)-Fenchyl Alcohol, Delta-3-Carene, 4-Allylanisole, beta-Caryophyllene. These compounds were identified with the assistance of GC-VUV analysis under identical conditions [17].

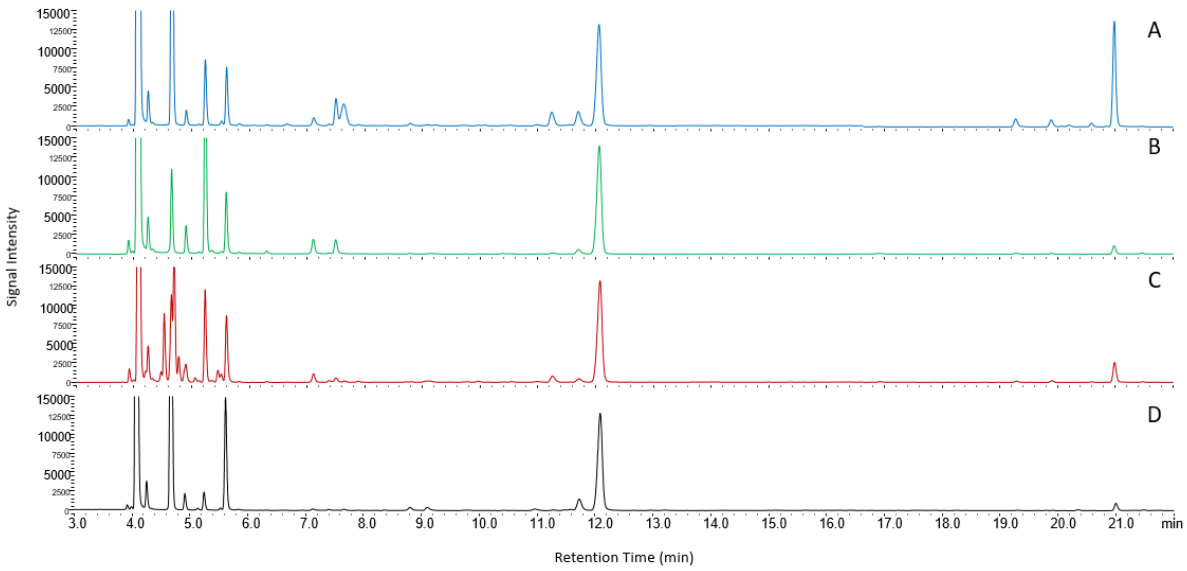

Figure 6-2. Chromatograms of four turnpentine oil samples. A) Sample A, B) Sample B, C) Sample C, D) Sample D.

Quantification of the terpenes compounds were based on equation 1 and the internal standard dodecane. Table 6-1 shows the quantification of the major terpenes identified. As shown in the table, α-pinene has the largest concentration that is presented in all the four samples. (-)-beta-Pinene has the second large portion in all the samples. The quantification results of the terpene closely matched the results from the GC-VUV quantification [17]. GC-Polyarc/FID analysis has saved a large amount of time and work compare to a regular calibration quantitative method. Only one sample with one internal standard was prepared with one triplicate run set, the results were simply calculated as showing in Table 6-1 based on equation 1. Reference spectra of each terpene was not needed prior to quantification, as with GC-VUV, but only the molecular formula. As showing in the table, other than the ones that have very small average, the rest have very low relative standard deviations that are tightly clustered around the average indicating that the determination has very good reproducibility too.

Table 6-1 Quantification of terpenes in the four turpentine oil samples in triplicates in order to get the average and relative standard deviation.

Compound	A (mg/ml)	B (mg/ml)	C (mg/ml)	D (mg/ml)
Alpha-Pinene	60.2 ± 0.67%	65.4 ± 0.6%	71.5 ± 0.6%	49.3 ± 1.6%
Camphene	1.2 ± 8.3%	1.1 ± 9.1%	1.8 ± 11.1%	1.13 ± 1.77%
(-)-beta-Pinene	14.5 ± 2.8%	3.01 ± 1.32%	3.59 ± 2.51%	28.08 ± 0.21%
Beta-Myrcene	0.63 ± 6.3%	0.999 ± 0.901%	1.077 ± 0.743%	0.672 ± 0.595%
p-Mentha-1,5-diene	0.038 ± 21.053%	0.04 ± 7.50%	0.020 ± 5.00%	0.073 ± 5.479%
Delta-3-Carene	2.74 ± 2.19%	11.65 ± 0.69%	3.78 ± 0.53%	0.77 ± 1.23%
d-Limonene	2.52 ± 1.59%	2.5 ± 0.4%	3.03 ± 0.33%	5.5 ± 12.7%
gamma-Terpinene	0.035 ± 8.571%	0.107 ± 3.738%	0.047 ± 6.383%	0.019 ± 21.053%
Terpinolene	0.48 ± 12.50%	0.79 ± 3.80%	0.485 ± 1.443	0.087 ± 6.897%
Linalool	1.81 ± 1.10%	0.862 ± 0.928%	0.323 ± 2.786%	0.007 ± 57.143%
(R)-Endo-(+)-Fenchyl Alcohol	0.072 ± 8.333%	-	0.076 ± 2.632%	0.021 ± 38.095%
Delta-3-Carene	1.162 ± 0.775%	0.076 ± 7.895%	0.55 ± 3.63%	0.048 ± 8.333%
4-Allylanisole	1.348 ± 0.148%	0.41 ± 2.44%	0.36 ± 5.56%	1.15 ± 2.61%
beta-Caryophyllene	0.038 ± 23.684%	-	0.040 ± 12.50%	-

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6.4.3 Quantification of Polyethylene glycols (PEGs).

Glycols analysis is challenging over quantification accuracy due to their high boiling points and poor peak shape on most low-polarity GC columns. Since applications using PEG are performed in solution and not at 300 °C, the desire is to accurately measure the condensed concentration. The Polyarc offers an avenue to monitor systematic loss through the chromatographic process through direct carbon quantification. The systematic loss for high MW PEG species throughout the GC process can be estimated through determining the loss measured using standards with similar retention characteristics. In this case, a series of aliphatic hydrocarbons from C_{12} to C_{40} were used. Accounting for this loss improves the accuracy of the cumulative PEG concentration in solution, indicating more accurate measurements for each PEG species. Three different PEG sample mixtures including PEG200, PEG300, and PEG400, which have the average molecular weight ranging from 200-400 g/mol were tested.

Figure 6-3-A shows the chromatograms of the three different chain length PEGs from GC-polyarc/FID system. PEG200 has shortest chain length polymers with the average molecular weight ranging from 190-210 g/mol, PEG300 has longer chain length polymers, and PEG400 has the longest chain length polymers ranging from 380-420 g/mol. Figure 6-3-B shows the adjusted concentrations of each PEG species within the PEG200, PEG300, and PEG400 mixtures associated with the aliphatic hydrocarbons. Quantitation based on equation 1 of each polymer species of the three PEG mixtures is noted in Table 6-2 as the “Measured” concentration. As stated earlier, these values were able to be determined without calibration of each species, but through a ratio of responses with the internal standard, n-decane. Recovery corrections due to chromatographic conditions were performed with a correction factor calculated from triplicate injections of the hydrocarbon standard under identical conditions immediately prior to each PEG mixture triplicate set, noted as “HC Rec” in Table 6-2. The adjusted concentrations of each species for the three mixtures are plotted in Figure 6-3-B. As expected, polymers of 12 and 13 EG monomers in PEG400 experienced a fair amount of system loss, as observed

through the recoveries of C_{38} and C_{40} of similar retention, respectively. Of PEG200, PEG300, and PEG400, the latter was the only species to experience a quantifiable loss of approximately 5% (90 µg on column) due to instrument conditions. That said, routine recovery adjustments may be more beneficial for higher MW polymers than these mixtures.

The Polyarc system successfully showed very sensitive detection of different chain length distribution polyethylene glycols with consuming less time and resources with regards to calibration and standard handling. Accurate quantification of each species leads to the improved average MW distribution labels and reaction monitoring during production. The FID equipped with the Polyarc was able to quantify each polymer of increasing chain length without the need to purchase the ten individual species monitored for this work.

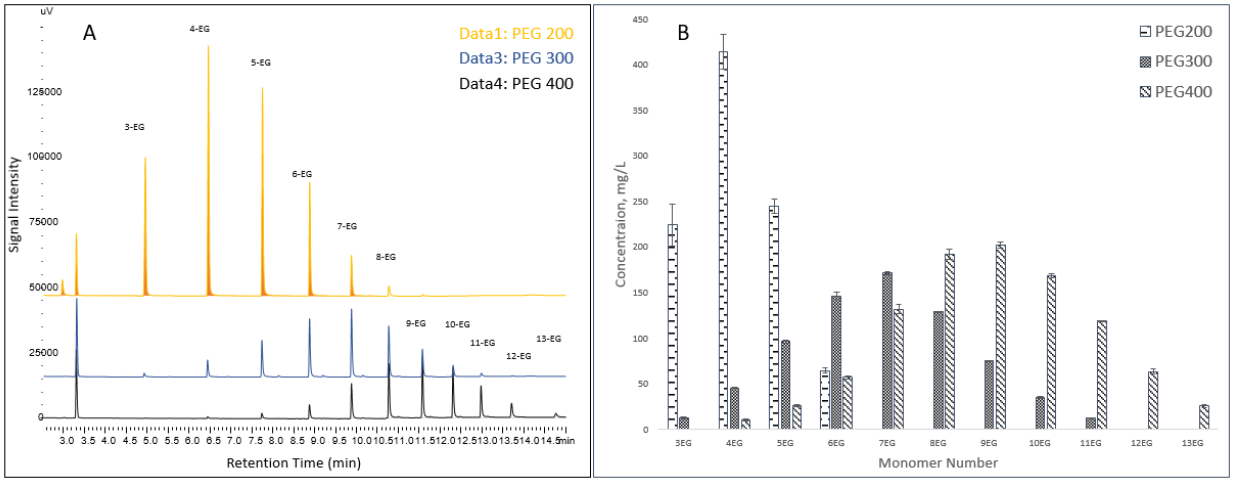

Figure 6-3. Quantification of PEGs. (PEG200, PEG300, PEG400). A) Chromatograms of PEG200, PEG300, PEG400 respectively. B) Adjusted concentrations of each PEG species within the PEG200, PEG300, and PEG400 mixtures

Table 6-2 Measured and Adjusted concentration (mg/L) of PEG species with each mixture. Recovery in the final column is based off an expected 900 mg/L PEG final concentration.

	3EG	4EG	5EG	6EG	7EG	8EG	9EG	10EG	11EG	12EG	13EG	Recovery
PEG200												
Measured	230	420	238	61								106 ± 6%
HC Rec	102.6%	101.8%	97.1%	95.3%								
Adj Conc	220	410	245	64								105 ± 5%
PEG300												
Measured	13	46.2	96	148	173	128.9	73.6	33	11.1			80.3 ± 0.8%
Rec	101.7%	101.7%	99.9%	101.2%	100.8%	100.2%	98.3%	95.5%	91.0%			
Adj Conc	12	45.9	96	146	171	128.6	74.9	35	12.2			80.2 ± 0.8%
PEG400												
Measured		10.1	25.1	55	127	185	195	160.	109.5	58	21	105 ± 3%
Rec		101.4%	96.9%	95.9%	96.5%	96.5%	96.8%	95.2%	92.3%	91.4%	81.5%	
Adj Conc		10.0	25.9	57	131	192	202	168	118.6	63	26	110 ± 3%

The accuracy of these measurements, i.e. 100% PEG recovery, were not of interest for this demonstration. What is made apparent through using the n-decane IS is deviation affecting accuracy must be found within the sample preparation, as the IS would experience the same degree of system loss. PEG200 and PEG400 contained 105 and 110% of the expected polymer concentration in solution, respectively, while PEG300 contained only 80% of the expected concentration. The resulting deviations most likely stemmed from the preparation from primary containers. Preparing calibration curves using these inaccurate stock solutions would have masked the erroneous values until premixed certified reference materials were compared to the fit line and found to be out of accuracy specification for the method.

6.4.4 Quantification of equimolar hydrocarbons from C6-C10

As mentioned above, the Polyarc microreactor coverts carbon atoms of volatile and semivolatile compounds to methane with two instantaneously reactions in tandem reaction chambers before the interface with the FID. The response signals eventually detected by the FID are methane for all the compounds, which enables the peak area of the compound equivalent to per carbon basis. With this introduced, we prepared a sample that contains seven equimolar aromatic and saturated hydrocarbons

ranging from C6-C12 including hexanes, cyclohexane, benzene, heptane, cycloheptane, toluene, octane, n-nonane, decane, naphthalene, undecane, dodecane, and 1,6-dimethylnaphthene to validate this concept and to check the full conversion of linear, cyclic and aromatic compounds.

Figure 6-4-A displays the chromatogram of the equimolar hydrocarbon mixture. In the figure, we can see that benzene and cyclohexane coelute, as do octane and cycloheptane, which explains the larger observed peak areas compared to other chromatographic peaks. When the total peak area was processed for each analyte's contribution, their response fell onto the trend line of similar responses across the equimolar compounds. In addition, due to the focusing issues and multiple hexanes, early elute hexane peaks have very bad shape. Other than these four analytes, the rest of the compounds all give nearly equal peak area which proved the assumption that the detector responded to the equimolar compounds equally. Figure 6-4-B shows the correlation between peak area and carbon numbers of the aromatic and saturated linear and cyclic compounds from the mixture. Other than the coeluting peaks and hexane, most of the compounds showed very similar peak areas which indicates the similarity of response. Furthermore, assuming the coeluting peaks of cyclohexane and benzene, cycloheptane and octane are the coelution of two methane signals from each component, then divided each of them by 2 should lead to the same peak area as others. As shown in the Figure 6-4-B, half of the intensity of the coeluting peaks are most likely equivalent to the peak area of rest of the analytes, which again proved that the Polyarc system has very desirable and accurate universal carbon sensitivity.

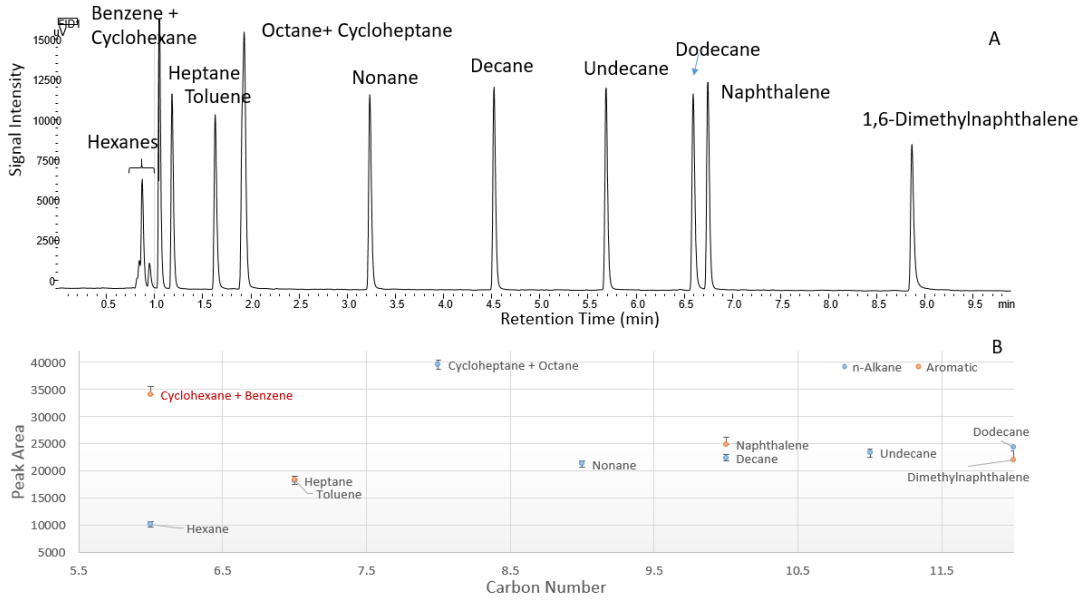

Figure 6-4. A) Chromatogram of the equimolar hydrocarbon mix. B) Correlation between peak areas and carbon numbers of aromatics and saturated hydrocarbons.

6.5 Conclusion

As one of the most important inventions in gas chromatography, the flame ionization detector is familiar and widely used despite inherent shortcomings operators have grown accustomed to managing. As an alternative for traditional FID, methanization has been introduced in this other works as a means of enhancing FID performance. It provides equal carbon response for all compounds and increased response for some compounds compared to traditional FID, which helps to significantly reduce the cost and labor needed for calibration and improves the accuracy of quantification. Here four different types of complex mixture samples have been quantified by the GC-Polyarc/FID system ranging from light hydrocarbons to terpene and polymer samples. Only one internal standard has been applied for each

sample analysis and no calibration process was involved. The quantification results obtained from this Polyarc system demonstrates very desirable accuracy of standards. The analysis of equimolar hydrocarbons furthermore validates the concept of the accurate uniform carbon response. The quantification of terpene mixture and polymer mixture confirm the ability of the Polyarc for analyzing samples that either have complex physical or structural properties or wide concentration range. Additional flexibility with the Polyarc system is possible through splitting the column flow prior to Polyarc to another detector such as a mass spectrometer.

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Chapter 7

Qualitative and Quantitative Analysis of Oxygenates in Gasoline using GC/VUV and GC/FID

7.1 Abstract

Oxygenates are the most important additives that have been used significantly in fuels in the past decades. Characterizing and monitoring the oxygenates components in fuels became very important in oil and fuel industries and environmental agencies. Many methods have been developed for oxygenates analysis but with limitations and disadvantages. In this research, gas chromatography-vacuum ultraviolet spectroscopy (GC-VUV) and gas chromatography-flame ionization detection (GC-FID), are applied to perform the oxygenates analysis. An ionic liquid column SLB ILD3606 was used which is specifically designed for the determination of benzene, other aromatics, and oxygenates in gasoline. The gas chromatography-vacuum ultraviolet spectroscopy was used to identify the oxygenate and deconvolute the coeluting compounds. The GC-FID was applied to quantified the oxygenates in three different gasoline samples. Excellent separation of oxygenates in complex gasoline sample was obtained by GC-VUV. Coeluting oxygenates like t-butanol, ethanol, and 2-propanpol are successfully deconvolved in gasoline sample. Accurate quantification results of oxygenates were obtained by GC-FID within 80-120% recovery.

7.2 Introduction

Gasoline is one of the energy products derived from petroleum refinery. It contains over 500 hydrocarbons from C3-C12 that can be classified into different groups including paraffins, isoparaffins, aromatics, naphthenes, and olefins [1, 2]. The engine combustion process efficiency, the emission of undesired gases are all depended on the composition in the fuels. In order to improve the engine performance and reduce emissions, different fuel additives are added to fuel products [3] [4]. Engine knocks have been a continuous problem since 1916. The knocks will make the engine work less smooth

and less efficient. Iodine has then been discovered initially that is added into engine to reduce the knocks by increasing octane. However, because of the disadvantages of iodine, for instance, it is corrosive to the engine and it is very costly, the use of iodine is therefore decreased[5]. Later on, scientists discovered an alternative additive, tetraethyl lead (TEL), which can also be used to reduce the engine knocking issue. It has then become more popular and been applied in a large amount of oil and gas companies [6]. Each gram of lead added to a gallon of gasoline can increase the octane rating by 10 times or more in octane numbers [7]. However, scientists have also discovered that with the high consumption of lead, the emitting of lead oxide would increase a lot and thus became at a very hazardous level. Therefore, the usage of lead additives has been controlled due to its negative impact to the public health and environment [6]. Oxygenates, oxygen containing organic compounds, has then become the most important additive in gasoline. Oxygenates that have been mostly used are C1 to C4 alcohols like methanol, ethanol and methyl ethers like methyl tert-butyl ether, (MTBE) and tert-amyl methyl ether (TAME) while propanols and butanols are primarily added as co-solvents [8, 9].

Oxygenates have been used significantly to increase the octane number to decrease the engine knocking and to reduce the toxic gases emission [5, 10]. They are very useful alternatives to the poisonous tetraethyl lead. Different from other hydrocarbons in gasoline, diesel or other fuel products, oxygenates contain oxygen that helps fuel to combust more completely due to the presence of oxygen. They not only improve the efficiency of engine combustion, also help on the reduction of greenhouse gas emission [11]. An addition of 10% ethanol blended in gasoline can largely reduce the CO emission [12]. Another advantage of using oxygenates as an alternative is that it is not only an octane booster, it also is a renewable resource [13]. Thus, characterizing and quantification of oxygenates components become a very crucial task among the oil and fuel industries and environmental investigations.

There are many different methods have been developed on oxygenates analysis that rely on purge-and-trap techniques, flame ionization detectors (FID), photoionization detectors (PID), or mass spectrometers(MS) [14-16] [17] [18]. PID and FID cannot provide specific signals, only retention time is available. Therefore, performing qualitative analysis on complex samples with these two techniques will be very difficult and challenging. In addition, because of the nonspecific detection, more errors will be introduced if the compounds that is interested in is coeluting with other peaks [14]. EPA method 8020

and 8021 utilizes the photoionization detector (PID), which is very sensitive to double bonds and halogenated but very less sensitive to oxygenates. In addition, it provides false-positive and inaccuracy results under certain conditions [14-16]. Thus, this is not a suitable method for oxygenates analysis in complex gasoline samples. EPA method 8015 applies a flame ionization detector (FID) to determine the various nonhalogenated volatile organic compounds and semivolatile organic compounds. Oxygenates can be detected but with very poor resolution. FID is a non-selective detector and it cannot handle the interference from many for other non-targeted compounds in a very complex sample [17]. Mass spectrometry provides more specific identifications. EPA method 8620 is a common method based on GC-MS analysis for oxygenates analysis in complex gasoline samples, which gives more confident and comprehensive results [18]. GCMS provides better determination on unidentified compounds but it still has problem on resolving coeluting species epically between oxygenates and other compounds [19]. American Society for Testing Materials method D4815 was then published for determination of C1 to C4 alcohols and MTBE in gasoline by gas chromatography, this method was design to investigate methanol, ethanol, and various ether oxygenates in finished gasoline [20]. In this method, two-dimensional column is needed to perform the separation. The first column is applied as a polar column where the oxygenates and heavier hydrocarbons will be retained and the lighter hydrocarbons do not retain and will be vented from the column. Switch valves are applied to control the flow direction. After switching the valve, the analytes are back flushed to a non-polar column to be separated and then detected by a FID detector [20]. This method vents off the light hydrocarbons during the initial chromatographic process, which makes it less desirable when it comes to total hydrocarbon analysis. Also, as it has been mention above, although FID provides strong signals, but it is nonspecific, other techniques are still required to assist the determination on target compounds. Multidimensional GC coupled to MS has also been developed to determine the oxygenate compounds and BTEX in gasoline simultaneously. It achieves very good correlation with results that have been obtained from the previous EPA and ASTM methods [21]. Though Multidimensional GC provides excellent separation and powerful resolution, there are still disadvantages. It can be less user-friendly and relatively harder to operate and maintain because of additional hardware and software requirements. Method development challenges include the optimization of the modulator, the modulation time, and the avoidance of wrap around. In addition, the capital equipment and

maintenance costs can be quite high. Therefore, Methods with excellent comprehensive separation with the minimal cost and operation technique needed are very necessary to be developed.

In this research, we introduced other alternative techniques that can also be applied to qualify and quantify oxygenates in complex gasoline samples. Vacuum ultraviolet spectroscopic absorption detector (VUV), a recent GC detector has been applied in this research to characterized oxygenates and deconvolve the coeluting analytes in gasoline. The vacuum ultraviolet detector (VUV) is a new non-destructive mass sensitive detector for gas chromatography that continuously and rapidly collects full wavelength range absorption between 120 and 240 nm [22, 23]. In the gas phase, every compounds including isomeric and isobaric species has their own unique absorption spectra [24, 25]. One of the major advantages of this detector is that it can deconvolve coeluting isomers where other most gas chromatographic detectors have problems[26]. GC-FID was used to perform the quantification of oxygenates in gasoline. In this research, a standard contains 16 oxygenates were analyzed on GC-VUV to identify the oxygenates eluting order. A gasoline sample was analyzed on both GC-VUV and GC-FID to evaluate the qualification and quantification ability of GC-VUV and GC-FID on oxygenates analysis in complex mixture compare to traditional methods.

7.3 Experimental

7.3.1 Instrumentation

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia MD) was coupled to a VGA-100 VUV detector (VUV Analytics, Inc., Cedar Park TX). The system was operated in the constant flow rate (2 mL/min) with helium carrier gas. The GC inlet temperature was set to 175 ◦C. The injection volume was 0.2 µL with 200:1 split ratio. The GC oven profile was set to start at 30 ◦C (held for 1.5 min) and then increased to 250 ◦C at a rate of 10 ◦C/min (held for 5 min). The transfer line and flow cell temperatures for the VUV detector were set to 275 ◦C, and the make-up gas (nitrogen) pressure was set to 0.25 psi. The data collection rate was set to 2.67 Hz.

A Shimadzu GC-2010 Plus gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD) outfitted with a flame ionization detector was used to perform the quantification analysis of

oxygenates. Helium was used as the carrier and FID makeup gas. FID flow settings consisted of 350 mL/min air, 1.5 mL/min hydrogen, and 20 mL/min helium makeup. The column used for the GC-VUV and GC-FID analysis is a SLB®-ILD3606 Column (30 m × 0.25 mm × 0.20 µm). The GC inlet temperature was set to 175 °C. The injection volume was 0.2 µL with 200 split ratio. The GC oven profile was set to start at 30 °C (held for 1.5 min) and then increased to 250 °C at a rate of 10 °C/min (held for 5 min).

7.3.2 Materials

An oxygenates standard from Supelco (Bellefonte, PA) was used to assist identifying the oxygenates in gasoline named D4815 qualitative peak ID mix. It contains Methanol 7.3 % (w/w), Ethanol 7.3 % (w/w), tert-Butanol 7.3 % (w/w), tert-Butyl methyl ether (MTBE) 4 % (w/w), tert-Butyl ethyl ether 4(ETBE) % (w/w), 2-Methyl-1-propanol 7.3 % (w/w), 2-Propanol 7.3 % (w/w), 1-Propanol 7.3 % (w/w), 2-Butanol 7.3 % (w/w), 1-Butanol 7.3 % (w/w), Benzene 5 % (w/w), Diisopropyl ether 4 % (w/w), tert-Amyl methyl ether(TAA) 7.3 % (w/w), 1,2-Dimethoxyethane 6 %(1,2-DME) (w/w). A gasoline sample was obtained from a random gas station. 4-Heptanol from Sigma-Aldrich (Milwaukee, WI) was used as the internal standard for all the quantification analysis. An oxygenates CRM standard from Restek (Bellefonte, PA) was diluted with pentane to 1% and 10% to evaluate the quantification accuracy of the methods including tert-Amyl ethyl ether (TAEE) (2,000 µg/mL), tert-Amyl methyl ether (TAME) (2,000 µg/mL), tert-Butanol (TBA) (10,000 µg/mL), Diisopropyl ether (DIPE) (2,000 µg/mL), Ethyl-tert-butyl ether (ETBE) (2,000 µg/mL), Methyl tert-butyl ether (MTBE) (2,000 µg/mL).

7.4 Results and Discussion

7.4.1 Qualitative analysis of Oxygenates using GC-VUV.

The GC-VUV in this research is applied as a qualification tool to identify the oxygenate eluting order which can be used in the following FID oxygenates analysis. Information of individual components can be readily obtained based on reference to a library of matched spectra. Since similar compounds exhibit similar absorbance features, VUV can qualitatively visualize the information according to defined

wavelength regions and further to deconvolute co-eluting species based on known reference spectra for the different analytes [26-28].

Figure 7-1 shows the separation of the oxygenates standard on GC-VUV with the SLB® -ILD3606 Column. The SLB-ILD3606 column contains an ionic liquid stationary phase and is specifically for the determination of benzene, other aromatics, and oxygenates in gasoline. Of note, the peak shapes for the oxygenates are of very high quality with this phase. In figure 7-1, it shows the separation of the oxygenate standard contains methanol, ethanol, tert-Butanol, MTBE, ETBE, 2-Methyl-1-propanol, 2-Propanol, 1-Propanol, 2-Butanol, 1-Butanol, Benzene, DIPE, TAME, 1,2-DME. Identification was performed by searching against the existing VUV library.

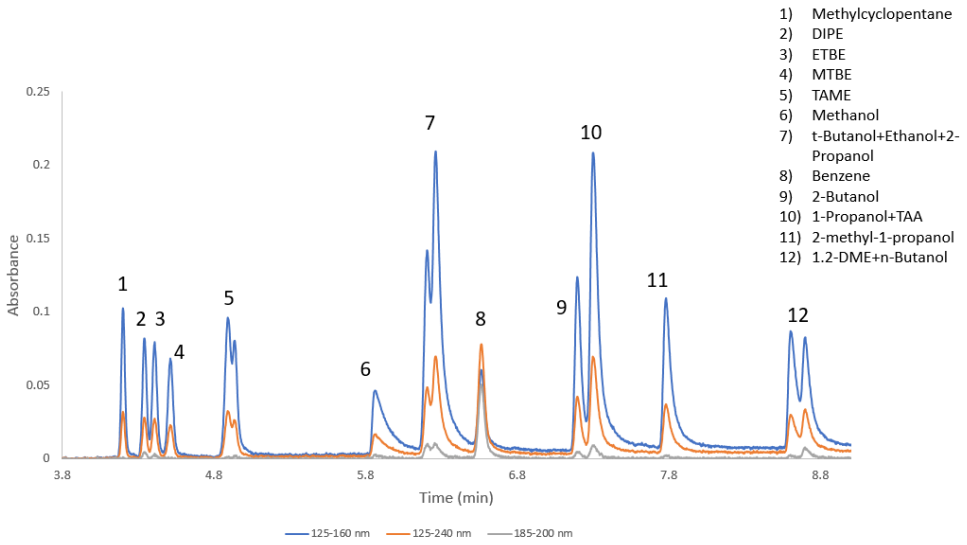

Figure 7-1. Separation of oxygenates standards with GC-VUV including methanol, ethanol, tert-Butanol, MTBE, ETBE, 2-Methyl-1-propanol, 2-Propanol, 1-Propanol, 2-Butanol, 1-Butanol, Benzene, DIPE, TAME, 1,2-DME.

In Figure 7-1, some coelution is apparent. t-Butanol, ethanol, and 2-propanol are coeluting together, 2-butanol, 1-propanol, and TAA are coeluting together, 1,2-DME and n-butanol are coeluting together. Also, the TAME has the interferences from the washing solvent dichloromethane (DCM). In

order to successfully separate all the individual compounds, a deconvolution method has been used which can separated all the coeluting peak simultaneously as showing in figure 7-2.

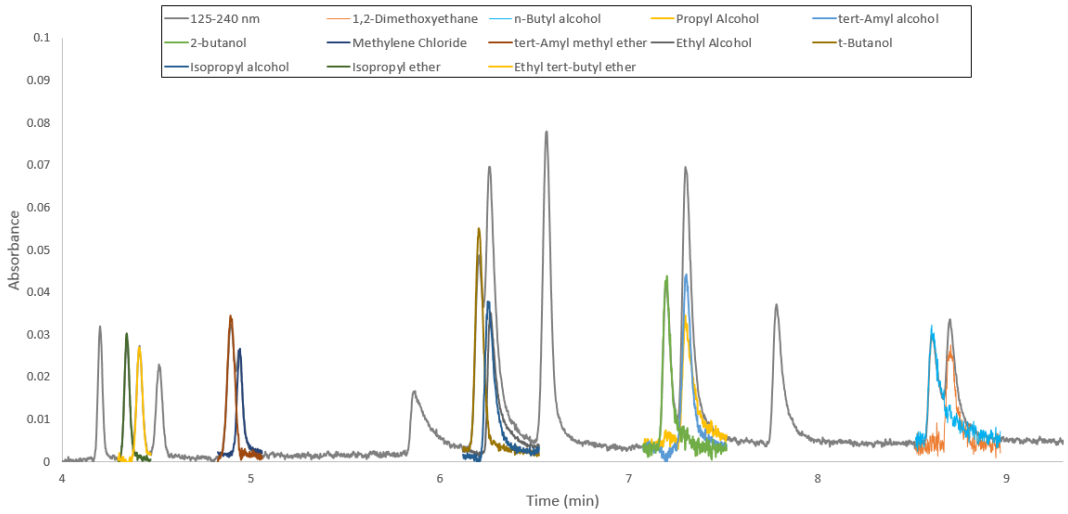

Figure 7-2. Deconvolution of coeluting oxygenates with GC-VUV.

The coeluting peaks have been successfully deconvolved into the individual peaks without any assistant of other techniques or setups. With this advantage, we moved forward to real complex gasoline samples analysis to see if it is possible to separate the oxygenate and deconvolve the coeluting compounds. A gasoline sample spiked with 10% oxygenates standard was analyzed on GC-VUV. Luckily, most of the oxygenates were all able to be identified and deconvolved. An example of oxygenates deconvoluting is showing in figure 7-3. It shows the deconvolution of coeluting ethanol, t-butanol, and 2-propanol.

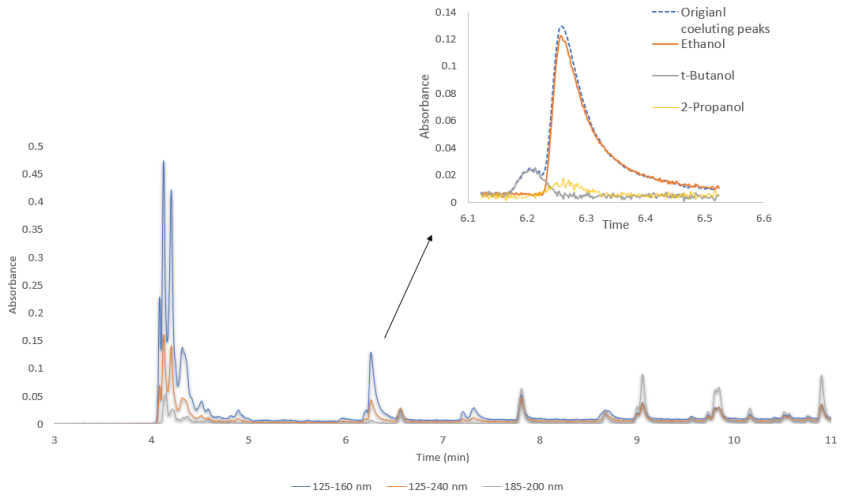

Figure 7-3. GC-VUV chromatogram of gasoline sample with 10% oxygenates standards spiked and the deconvolution of coeluting oxygenates of ethanol, t-butanol, and 2-propanol.

The results we have showed here proved that with the use of GC-VUV and the SLB® -ILD3606 column, it was able to separate oxygenates and heavier hydrocarbons from the light hydrocarbons that does not retain on this polar ionic liquid column. Furthermore, it showed the capability of GC-VUV on deconvolution of the coeluting oxygenates without other multidimension instruments.

7.4.2 Quantitative analysis of Oxygenates on GC-FID

The GC-FID in this research is applied to quantify the oxygenates in gasoline sample. Internal standard calibration method was used for the quantification analysis. The oxygenates standard was diluted with pentane to 7 different concentrations: 0%, 0.1%, 0.5%, 1%, 2%, 5%, and 10%. The internal standard used in this research was 4-Heptanone with the concentration of 5% in each sample. The individual concentration of each analyte presented in the each different samples are calculated from their original concentration to make the calibration curve. Figure 7-4 shows the calibration curves for all the oxygenates in the standard. X-axis presents the concentration of the oxygenates and the y-axis presents

the ratio of peak area between the analytes and the internal standard. All the analytes have very good linearity of the calibration data which can be further applied to quantify the oxygenates in real gasoline sample.

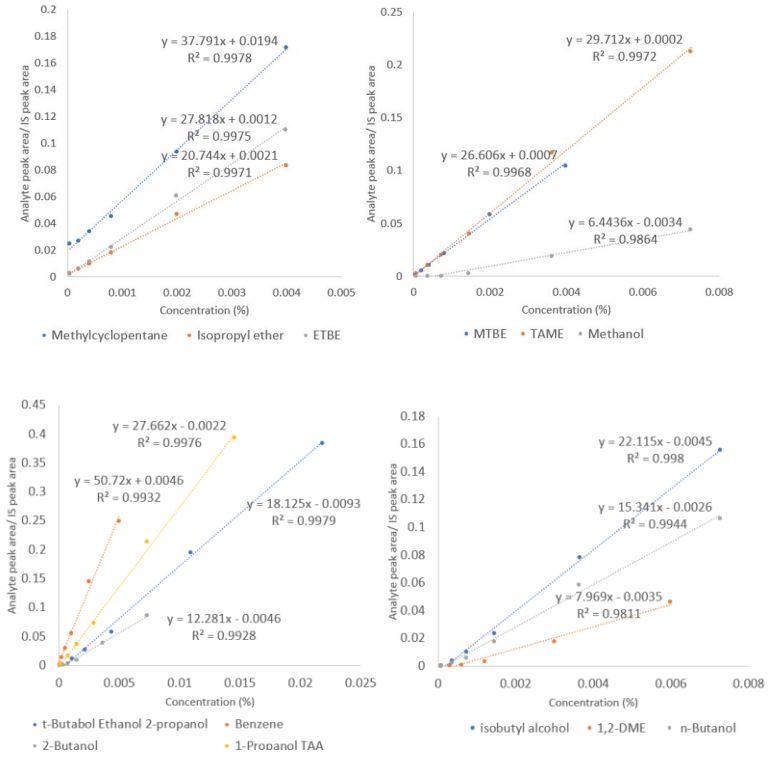

Figure 7-4 Calibration curves for all the oxygenates in the oxygenate standard.

An oxygenates CRM standard contains TAEE, TAME, tert-Butanol, DIPE, ETBE, MTBE in methanol was used to evaluate the quantification accuracy of this method with the original concentration of 0.2%, 0.2%, 1%, 0.2% 0.2%, 0.2%, and 98% respectively. Only DIPE, MTBE, TAME, methanol is compared since the rest are not presented in the oxygenates standard. 1% of the CRM standard was prepared in pentane with 5% internal standard 4-heptanone. The sample is analyzed on GC-FID and the concentration is calculated based on the internal standard calibration. Results are showing in table 7-1.

Table 7-1. Recovery calculation of oxygenates in CRM standard based on the internal standard calibration.

Analyte		CRM 1%	
	Initial Conc. %	Recovered Conc.%	Conc. Rec.%
DIPE	0.002	0.0019 ± 0.0004	93.6
MTBE	0.002	0.0016 ± 0.0004	80.8
TAME	0.002	0.0018 ±0.0002	92.4
Methanol	0.980	1.03 ± 0.01	105.3

The initial concentration of each analyte after dilution is presented in table 7-1 as each of them has only 1% in the sample. The concentrations of the DIPE, MTBE, TAME and Methanol are calculated based their individual calibration curve obtained above. Satisfactory recovery of each oxygenate is obtained which indicated the accuracy of the internal standard method.

A random real gasoline sample is then analyzed on GC-FID to evaluate its ability on characterizing and quantifying the oxygenates in complex sample. Table 7-2 shows the recovery of the oxygenates spiked in gasoline sample. Sample A is the gasoline sample with only the 5% internal standard added. Sample A1 is the gasoline sample with 5% internal standard and 10% of the oxygenates standard added. This method is based on the spike recovery where the known number of analytes are spiked into the gasoline sample matrix and its response is measured. The response of the same analytes in the original gasoline sample matrix are also measured. The differences between the responses of the analytes are obtained to calculate the recovery of the oxygenates spiked in the gasoline based on the calibration curves obtained previously. The chromatograms of the gasoline samples are integrated and the peak areas ratios of the analytes to the internal standards form both samples are showing in the table. The recovery was then calculated based on the internal standard calibration curve of each analytes.

Table 7-2. Recovery calculation of spiked oxygenates in real gasoline sample based on the internal standard calibration.

	Initial Conc. %	Peak area ratio of A	Peak area ratio of A1	Peak area ratio of A1-A	Spike Recovery %	Recovery %
Methylcyclopentane	0.399	8 ± 1	7.3 ± 0.4	-1.25	-	-
Isopropyl ether	0.399	4.4 ± 0.6	4.0 ± 0.2	-0.4	-	-
ETBE	0.389	0.25 ± 0.08	0.35 ± 0.05	0.1	0.30	88.10
MTBE	0.389	0.25 ± 0.03	0.315 ± 0.008	0.07	0.30	67.20
TAME	0.726	0.04 ± 0.01	0.26 ± 0,03	0.22	0.70	102.00
Methanol	0.725	0 ± 0	0.03 ± 0.03	0.03	0.50	75.80
t-Butabol+Ethanol+2-propanol	2.170	1.4 ± 0.2	1.74 ± 0.02	0.34	1.90	89.80
Benzene	0.497	0.39 ± 0.06	0.58 ± 0.05	0.19	0.40	75.20
2-Butanol	0.727	0.005 ± 0.001	0.111 ± 0.005	0.11	0.90	123.00
1-Propanol+ TAA	1.453	0.009 ± 0.002	0.27 ± 0.08	0.26	1.00	66.40
isobutyl alcohol	0.727	0 ± 0	0.13 ± 0.02	0.13		84.80
1,2-DME	0.598	0 ± 0	0.044 ± 0.006	0.04	0.60	99.20
n-Butanol	0.726	0 ± 0	0.090 ± 0.004	0.09	0.60	82.10

As showing in the table, methylcyclopentane and isopropyl ether was not able to be determined because they came out together along with the light hydrocarbons. Too much of the interferences from the beginning light hydrocarbons covered up these two analytes that makes it unable to be determined. The rest of the oxygenates were successfully quantified. Most of the oxygenates have very excellent concentration recovery within 80-120% recovery. The recovery of MTBE, 1-propanol, TAA, and 2-butanol has more than 20% losses in the recovery. It is most probably due to the interferences from the matrix that are not able to be characterized.

7.5 Conclusion

A 16 component mixture of oxygenates including ethers and alcohols commonly added to fuels was qualified using the GC-VUV system and quantified using the GC-FID system. The separation was enhanced by the SLB ILD3606 column. The GC-VUV provided very excellent separation of oxygenates and deconvolution of the coeluting species in complex gasoline samples without extra techniques and instrument setups. High accuracy quantification of oxygenates within 80-120% recovery in complex gasoline sample is obtained from GC-FID. The qualification results obtained from the GC-VUV system demonstrates very desirable separation of oxygenates in complex gasoline sample and the quantification results obtained from GC-FID demonstrates very desirable accuracy of the quantification method. Therefore, combining the GC-VUV and GC-FID systems would be an excellent approach on oxygenates analysis in gasoline compare to other ASTM and EPA methods.

7.6 References

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Chapter 8

Summary and Future Work

As a very crucial energy resource, fossil fuel has received significant attention in a wide range of research fields. The composition of fuel products is very critical to their performance and value. Separation and identification methods for fuel products are very necessary to optimize the conversion of raw crude oil into different high value products, to predict their performance, and determine their quality. Gas chromatography is the most important technique in analytical research and GC–MS has been the gold standard for combined qualitative and quantitative analysis of volatile and semi-volatile compounds for many years. Many technologies and methods have been developed for oil and gas analysis. Though there are many methods for different applications, new methods and techniques are always needed for improving the separation and detection to overcome the limitations. The scope of this work was to demonstrate a set of new methods for both qualitative and quantitative analysis of different oil and gas samples, ranging from permanent gases to gasoline, and diesel fuels. In addition, to demonstrate the exploration and evaluation of new detectors on hydrocarbon complex mixture analysis for oil and gas industries.

Gas chromatography has continuously played an important role in gas sample analysis. Different detectors can be applied for gas analysis, but there are significant limitations for the detection of low mass gas compounds. In this research, gas samples from source of modern world and energy industry have been analyzed to demonstrate the use of GC–VUV as a new tool for small molecule gas analysis. Characterization of natural gas, natural gas in the headspace of collected groundwater, and the evolution of gases from thermal runaway events in Li-ion and Li-metal batteries were performed by GC-VUV. Reliable detection of gaseous components in these samples was achieved. C1–C5 linear and branched hydrocarbons, water, oxygen, and nitrogen were separated and detected in natural gas and the headspace of natural gas-contaminated water samples. Flammable and toxic gases like methane, ethylene, chloromethane, dimethyl ether, 1,3-butadiene, CS2, and methylproprionate from lithium batteries off-gassing were separated and deconvolved by GC-VUV. This research showed the capability

of GC–VUV for solving challenging analytical problems related to permanent gases, as well as volatile and semi-volatile compounds.

One of the limitation of the permanent gas analysis research is that the preliminary determination did not provide any quantitative analysis. Thus, we have further developed the pseudo-absolute quantitative analysis method. This new quantification method was performed by GC-VUV with a calibrationelss approach. It offers a routine quantification approach that largely reduces the time and work required for batch calibration involved quantification analysis and helps to experimentally evaluate the sources of sample loss and gain associated with sample introduction into a typical gas chromatography. Natural gas was then able to be both qualified and quantified which proved the capability of GC-VUV as a versatile tool on gas analysis. Benzene was also analyzed by applying this quantification method to validate its accuracy and to diagnose the systematic errors that could be introduced into the absolute mass of an analyte delivered on column. More practices still need to be performed on validation of the scope of this method including its linearity, limit of detection, and accuracy and precision at a wide range concentration levels. Various applications should also be performed to compare the accuracy and precision of this method to the traditional calibration methods.

Various methods are also available nowadays for gasoline and diesel analysis. Though there are many methods available, as one moves to heavier fuels, the number of available methods are limited. New methods on characterizing fuel products including gasoline and diesel are developed in this research by applying GC-VUV. Oxygenates including ethers and alcohols in gasoline were qualified using the GC-VUV system and quantified using the GC-FID system. The GC-VUV provided very excellent separation of oxygenates and deconvolution of the coeluting species in complex gasoline samples without extra techniques and instrument setups. High accuracy quantification of oxygenates in complex gasoline sample is also obtained by GC-FID. Method was also developed on GC-VUV to identify different classes of compounds and biomarkers in complex diesel fuel and artificially weathered diesel fuel mixtures. The use of different spectra filters made it possible to automatically classify different group of compounds in complex mixtures within a very simple approach. The use of the deconvolution technique further assisted

to separate coeluting species without any other multidimension columns and detectors. One issue is that the complexity of higher carbon species in diesel samples and other complex mixtures makes it very difficult for banking individual spectra for all the components. For example, the library has limited amount of C10-C12 naphthenes population that can affect the accuracy of the analysis of heavier samples that contain large amount of naphathenes. Thus, efforts are still needed to improve the qualification ability of GC-VUV for complex mixtures by expanding the VUV library cooperated with computational means. Future work regarding many different complex fuel applications would then be able to be performed with more powerful and comprehensive results. Furthermore, Coupling VUV with more advanced technique like GCxGC will be a great application that can certainly provide much more detailed separation of complex mixtures.

Appendix A

Supplementary Information for Comparison of GC-VUV, GC-FID, and Comprehensive Two-Dimensional GC-MS for the Characterization of Weathered and Unweathered Diesel Fuels

This supplementary information includes the normalized spectra for benzene, Ethylbenzene, n-Pentylbenzene, n-Hexylbenzene, Pentamethylbenzen to help gauge the contributions to responses in different wavelength regions, which can be expected from such analytes.

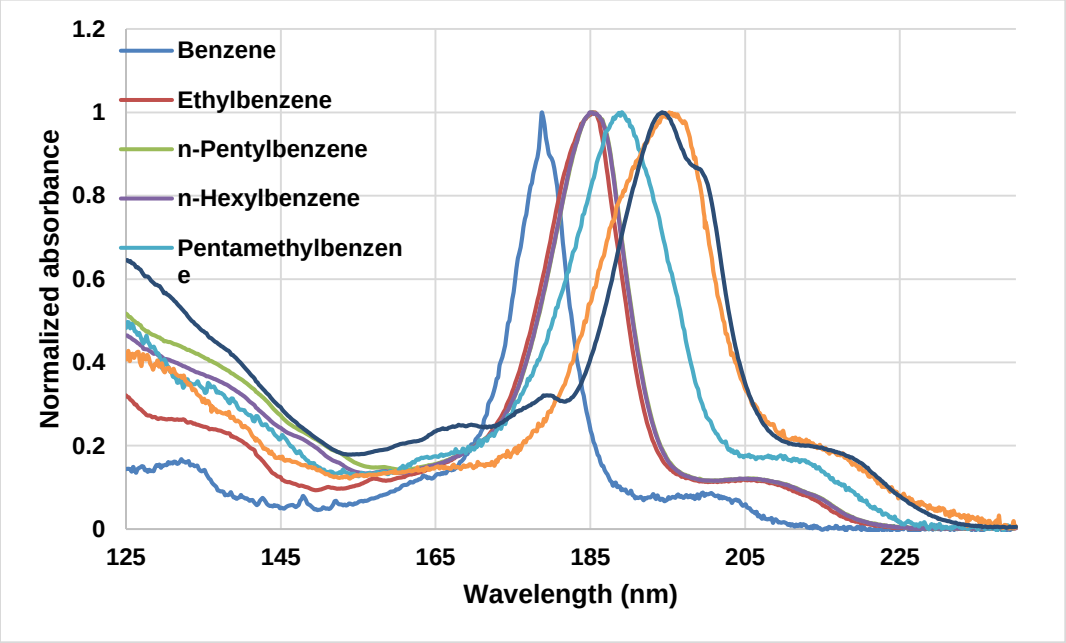

Figure S1. Normalized spectra for benzene Ethylbenzene, n-Pentylbenzene, n-Hexylbenzene, Pentamethylbenzen

Biographical Information

Ling obtained her Bachelor of Science degree in Chemistry from the Xuchang University in China in May of 2013. She later got accepted by the university of Texas at Arlington in Unites states as a graduate student. She joined Dr. Kevin Schug's Analytical Chemistry lab to work on development of qualitative and quantitative applications in energy industry using gas chromatography- vacuum ultraviolet spectroscopy.

During her graduate program in Dr. Kevin Schug's lab, she has acquired significant amount of knowledge and skills on analytical chemistry. She has dedicated herself on evaluating the new detector- vacuum ultraviolet spectroscopy, which has first been released by VUV Analytics, Inc. (Cedar Park, TX) in 2014. Her projects were focused on characterizing the qualitative and quantitative ability of GC-VUV for oil and gas products analysis. Her major contribution was developing methods to characterize very complex fuel samples like gasoline and diesel with GC-VUV. She has proved that GC-VUV can be a viable alternative to more complicated multidimensional GC for characterizing complex samples. Ling has grown immensely in her time as a Ph.D. student, her analytical skills on GC have become excellent due to her strong motivation and practice.

She graduates with her Ph.D. degree in Analytical Chemistry from the University of Texas at Arlington in November 2017. She plans to start a career related to energy and pharmaceutical industries.