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Determination of Hydrocarbon Group-Type of Diesel Fuels by Gas Chromatography with Vacuum Ultraviolet Detection

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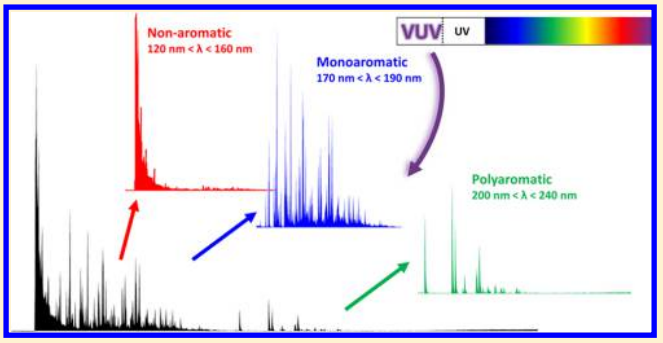
Supporting Information

ABSTRACT: A GC-vacuum ultraviolet (UV) method to perform group-type separations of diesel range fuels was developed. The method relies on an ionic liquid column to separate diesel samples into saturates, mono-, di-, and polyaromatics by gas chromatography, with selective detection via vacuum UV absorption spectroscopy. Vacuum UV detection was necessary to solve a coelution between saturates and monoaromatics. The method was used to measure group-type composition of 10 oilsands-derived Synfuel light diesel samples, 3 Syncrude light gas oils, and 1 quality control sample. The gas chromatography (GC)-vacuum UV results for the Synfuel samples were similar (absolute % error of 0.8) to historical results from the supercritical fluid chromatography (SFC) analysis. For the light gas oils, discrepancies were noted between SFC results and GC-vacuum UV results; however, these samples are known to be challenging to quantify by SFC-flame ionization detector (FID) due to incomplete resolution between the saturate/monoaromatic and/or monoaromatic/diaromatic group types when applied to samples heavier than diesel (i.e., having a larger fraction of higher molecular weight species). The quality control sample also performed well when comparing both methods (absolute % error of 0.2) and the results agreed within error for saturates, mono- and polyaromatics.



Middle-distillate fuels, including diesel and jet fuels, provide the bulk of the energy requirements for commercial transportation (truck, rail, and aviation), construction, and agriculture. Performance and emission properties of petrodiesel such as cetane number and exhaust emissions are linked to the total aromatic and polycyclic aromatic content of the fuel, and the aromatic content of diesel is regulated in some jurisdictions.[1−7] Measurement and characterization of aromatic content is necessary for process and quality control of diesel (and diesel-like fuel) production and to meet regulatory requirements.

The American Society for Testing Materials (ASTM) method D-5186-03 is a method specified for the determination of aromatic and polycyclic aromatic hydrocarbon (PAH, two or more aromatic rings) content of diesel and aviation turbine fuels.[8] The Canadian General Standards Board (CGSB) method CAN/CGSB-3.0 No. 15.0-94 is a determination of aromatic hydrocarbons by their ring number (one, two, or three aromatic rings) in middle distillate fuels.[9] Both the ASTM and CGSB methods specify the use of supercritical fluid chromatography (SFC) with a carbon dioxide mobile phase to separate diesel fuels according to group-type, after which they are detected using flame ionization detection (FID). Unfortunately, the SFC equipment specified cannot handle diesel samples that contain biodiesel, which are increasingly important biologically derived sources of fuel that may be used on their own or blended with conventional petroleum diesel fuels (petrodiesel). The 2011 Canadian requirement to add 2% biodiesel content to diesel fuel has complicated the use of these standard protocols as the biodiesel component does not readily elute from the SFC column. This leads to incorrect analytical results and fouling of the SFC column. Recently, ASTM has struck a working group to develop methods for petroleum analysis based on GC-vacuum UV technology, the goal being to provide alternate methods for petroleum separations that are more robust than existing methods.

Group-type separations of diesel fuels have been performed with gas chromatography (GC),[10−13] high-performance liquid chromatography (HPLC),[14−18] LC-GC,[19,20] SFC-GC,[21] SFC-MS,[22] and recently a number of hyphenated techniques have been reviewed.[23−25] Most commonly used HPLC detectors yield a nonuniform response for saturates and aromatics,[11,26−28] mandating the use of complex calibrations. However, the use of an FID provides reliable mass quantification of the different hydrocarbon group-types.[11,26−28] When more complex hyphenated techniques are used, reliable quantification becomes more difficult, especially when mass spectrometric detectors are used, as they too give nonuniform responses in group-type

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separations.[11] Finally, it should be noted that for group-type separations, the ultimate goal is not the separation and quantification of each individual compound but the quantification of families of compounds eluting in distinct regions so that the relative proportion of each family of compounds can be determined.

Ionic liquid (IL) stationary phases for GC exhibit several properties that show great potential for petroleum separations, including unique selectivity for polyaromatic hydrocarbons over aliphatic compounds and much higher thermal stabilities than conventional polar phases.[29−32] Ionic liquid columns have also been shown to be capable of separating fatty acid methyl ester (FAMEs) found in biodiesels without fouling the column.[33−36]

In order to have accurate diesel group-type determinations, high aromatic group-type resolution is necessary, while maintaining the resolution of saturates and aromatics.[11] To achieve the best group-based separation possible, several IL columns offering different phase chemistries were studied. The columns were assessed primarily on the basis of whether they could achieve high resolution between different hydrocarbon groups: saturates, mono-, di-, tri-, and polyaromatics. It was observed that diaromatics and larger could be fully separated from saturates, but another tool was necessary for distinguishing saturates from monoaromatics. One relatively simple way to do this is by selective detection.

A benchtop vacuum ultraviolet detector (vacuum UV) has been recently developed and tested.[37] This instrument allows collection of gas phase absorption spectra in the range of 115−240 nm. Using this range of wavelengths it is possible to probe the vast majority of compounds, not just those traditionally probed by UV absorption (λ > 190 nm). Interestingly, almost every chemical compound is reported to absorb in the vacuum UV spectral range (115−185 nm).[37] An added benefit of this type of system is that it also provides the user with full absorption spectra at every point in time during a separation, leading to useful qualitative data. All compounds eluted from the GC are transferred to the vacuum UV detector where they enter the flow cell. The flow cell has a set path length of 10 cm and a volume of 80 μL and has a makeup gas flow introduced before the flow cell, which is responsible for altering the residence time of the analyte molecules. A charge-coupled device (CCD)-equipped spectrometer is used to collect full-range absorbance spectra at a rate of anywhere between 2 and 100 Hz as analytes elute from the GC column. Vacuum UV is a powerful detection method that can detect volatile and semivolatile compounds which may be closely related. In this work, the vacuum UV system will be used to differentiate multiple overlapping signals and determine the weight percent of the group types, while providing an additional dimension of separation based on absorption spectra.

EXPERIMENTAL SECTION

Model compounds used for evaluating separation conditions consisted of docosane (Sigma-Aldrich, Oakville, Ontario, Canada), ethyl toluene (Sigma-Aldrich), tetralin (Caledon, Georgetown, Ontario, Canada), naphthalene (Fisher Scientific, Ottawa, Ontario, Canada), dibenzothiophene (Sigma-Aldrich), anthracene (Eastman, Mississauga, Ontario, Canada), pyrene (Sigma-Aldrich), toluene (Fisher Scientific), ethylbenzene (Fisher Scientific), and para-xylene (Fisher Scientific). Model compound samples (SFC 10 mix) were prepared by dissolving each compound in ACS grade carbon disulfide (Fisher Scientific) at room temperature.

A collection of ten Syncrude diesel samples (Syncrude Research Ltd., Edmonton, Alberta, Canada) with varying aromatic content were also tested: Fuels 1, 2, and 6−13. Three Syncrude light gas oil samples were also tested: Fuels 3−5. A Syncrude quality control (QC) sample (well-characterized diesel) was also used. All diesel/light gas oil samples were run without dilution. SFC results reported were provided by our collaborators who had previously had the samples analyzed by an accredited contract laboratory according to ASTM and CGSB methods.

Initial experiments were conducted on a 6890 GC (Agilent Technologies, Mississauga, ON, Canada) using helium as a carrier gas at a linear velocity of ∼30 cm s^{-1}. This instrument was equipped with an Agilent 7683 auto sampler (Agilent Technologies). The injector and detector temperature were set to 10 °C below the maximum temperature for each column. Detection was via flame ionization detection (FID). For the SFC-10 standard mixture, an injection volume of 1 μL was used with a split ratio of 20:1. Diesel samples were injected neat with a volume of 0.2 μL and a split ratio of 60:1. Data were analyzed using Chemstation (Agilent).

The IL columns studied (SLBIL-59, -61, -76, -82, -100, and -111) were all 30 m × 250 μm with 0.2 μm films, provided by Supelco (Oakville, Ontario, Canada). All GC-vacuum UV experiments were conducted on the same 6890 GC with a VGA-100 vacuum UV absorption spectroscopy detector (VUV Analytics, Inc., Cedar Park, TX) added for detection. All GC-vacuum UV studies were conducted on the IL-111 column 30 m × 250 μm with 0.2 μm film thickness. The injector temperature was set to 250 °C. An injection volume of 0.2 μL was used with a split ratio of 60:1. The detector transfer line and flow cell were kept at 300 °C. Data were analyzed using VGA-100 software (VUV Analytics, Inc.).

RESULTS AND DISCUSSION

To determine which column would give the best group-type resolution, initial testing was completed on six different IL columns (SLBIL-59, -61, -76, -82, -100, and -111) using the SFC 10 standard mixture and GC-FID. Different columns were compared on the basis of their group-type resolution. In comparing six different IL columns, it was found that only IL-100 and IL-111 were able to separate the saturate compounds from the diaromatic compounds, using any feasible separation

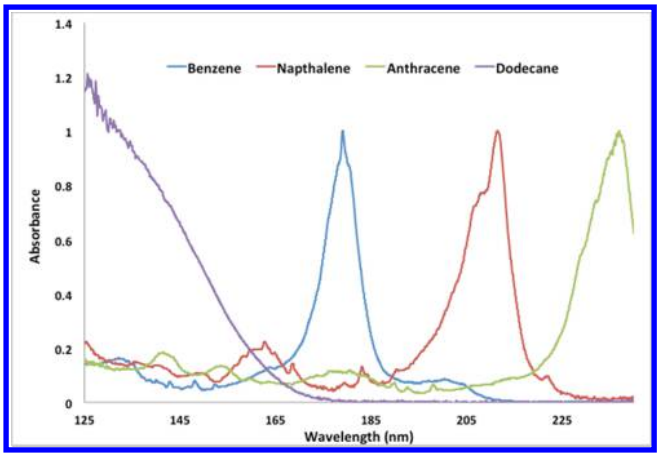

Figure 1. Vacuum UV Library[39] absorbance spectra for benzene, napthalene, anthracene, and dodecane.

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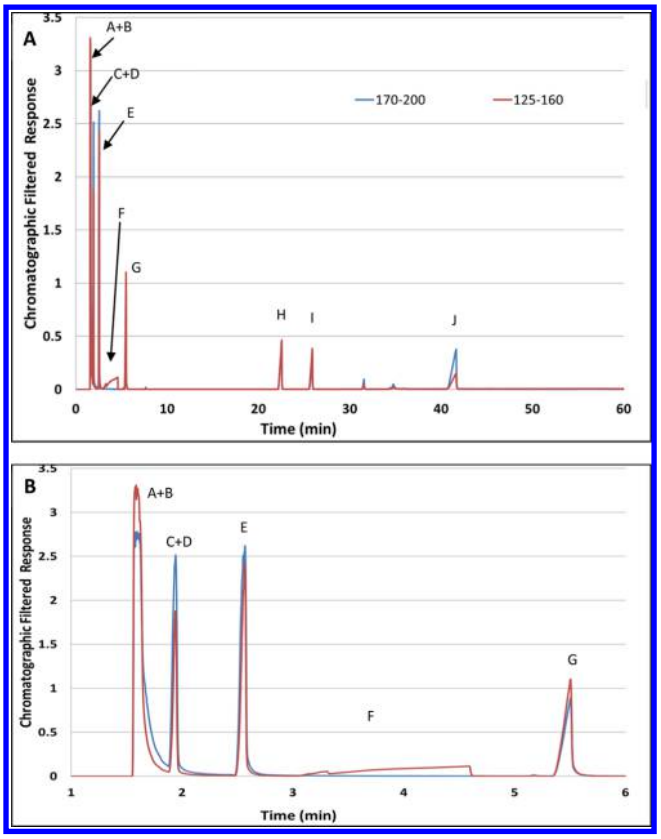

Figure 2. GC-vacuum UV separation of SFC-10 Standard Mix: (A) full chromatogram and (B) expanded region from 1−6 min. Blue trace is "aromatics" filter (average response over 170 nm < λ < 200 nm); red trace is "saturates" filter (average response over 125 nm < λ < 160 nm). Peak identification: A, benzene; B, toluene; C, ethyl-toluene; D, *p*-xylene; E, tetralin; F, docosane; G, naphthalene; H, dibenzothiophene; I, anthracene; J, pyrene. Note: two small peaks between I and J are contaminants.

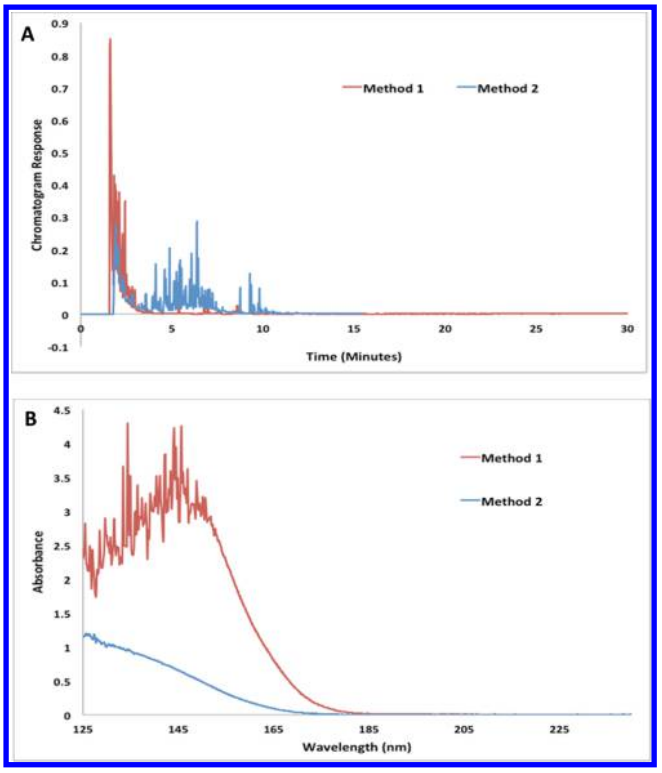

Figure 3. (A) GC-vacuum UV separation of Fuel 7 sample using Method 1 (red): 120 °C (0 min hold), 3 °C/min to 210 °C (5 min hold) and Method 2 (blue) 60 °C (3 min hold), 20 °C/min to 210 °C (0 min hold). Method 1 was the FID-optimized method. Method 2 was developed due to detector saturation. (B) Vacuum UV absorbance spectra collected at 2.2 min from chromatograms in part A. The noisy plateau in the spectrum from the Method 1 trace clearly indicates saturation of the absorbance signal at the shortest wavelengths.

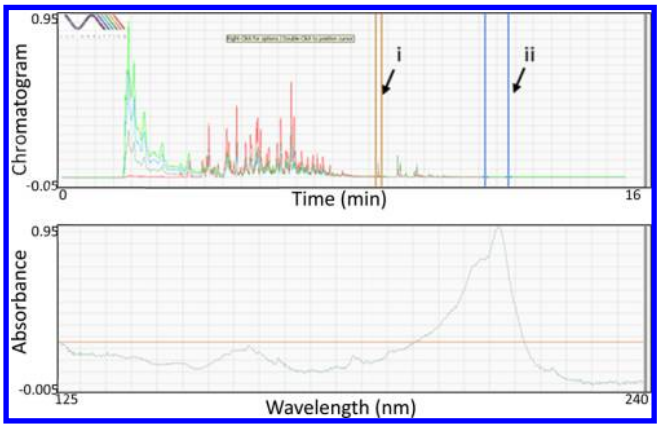

Figure 4. VGA-100 Data for Fuel 7 separation: (top) vacuum UV chromatogram display window; gray trace is total spectrum (125 nm < λ < 240 nm), red trace is aromatic filter (170 nm < λ < 200 nm), green is saturate filter (125 nm < λ < 160 nm), blue is a default filter (140 nm < λ < 160 nm) calculated by the software (not used in this research). (Bottom) Experimental average, background-corrected vacuum UV spectrum for selected region (i), where (ii) is the region selected for the background.

conditions, with SLBIL-111 providing the best resolution for saturates versus diaromatics (data not shown). Similarly, Krupcik et al. found that these two IL columns were useful for quantitative analysis of BTEX (benzene, toluene, ethylbenzene, and xylenes) samples.[38] Remaining experiments were completed using SLBIL-111. A ramp rate of 20 °C min^{-1} with a start temperature of 120 °C and no initial hold time provided the best group-type separation in the least amount of time. However, the IL column alone was unable to fully separate the saturate and monoaromatic compounds; thus, selective detection in the form of the vacuum UV was necessary. Initial experiments with the VGA-100 detector used the separation conditions optimized on the GC-FID.

Figure 1 depicts library spectra[39] of example saturated, one-, two-, and three-ring aromatics. This points to the possibility of using spectral filtering of data to differentiate saturates which absorb little at λ > ~170 nm from aromatic compounds which exhibit maxima in their absorbance spectra at λ > 170 nm. Further, the number of aromatic rings can also be determined based on the position of λ_{max}, which shifts to longer wavelengths as the number of rings increases.

To test the spectral filtering technique, the SFC 10 standard mix (docosane, ethyl toluene, tetralin, naphthalene, dibenzothiophene, anthracene, pyrene, toluene, ethylbenzene, and paraxylene) was analyzed and the resulting chromatogram examined using different wavelength filters. Figure 2 displays the chromatogram filtered with the so-called "aromatics" filter (blue), represented by the average absorbance over the 170 nm < λ < 200 nm range, while the red line shows the "saturates" filter which is a plot of the average response over 125 nm < λ < 160 nm. The expanded region depicted in Figure 2B shows the

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Table 1. Comparison of SFC Results for Fuel 7 Group-Type Weight Percent Determinations to GC-Vacuum UV Analyses with Different Temperature Programming Rates as Well as a Standard Addition Method, Run with the 5 °C min^{-1} Ramp

technique	saturate %	monoaromatic %	diaromatic %	polyaromatic %
SFC	64.6	32.4	3	0
vacuum UV 20 °C min^{-1}	67.6	28.0	4.5	0
vacuum UV 5 °C min^{-1} replicate 1	63.4	34.2	2.6	0.2
vacuum UV 5 °C min^{-1} replicate 2	64.2	33.8	2.9	0.2
standard addition	64.2	33.5	2.1	0.09

Table 2. GC-Vacuum UV Results for Group-Type Determination of Fuel 7 Using Dynamic Spectral Filtering

technique	saturate %	monoaromatic %	diaromatic %	polyaromatic %
SFC	64.6	32.4	3	0
vacuum UV dynamic processing replicate 1	63.6	34.2	2.2	0
vacuum UV dynamic processing replicate 2	64.6	32.4	3.0	0

Table 3. GC-Vacuum UV Results for Group-Type Determinations of Diesel and LGO Samples Using Dynamic Spectral Filtering ± Standard Deviation, $n = 3$

sample	saturates %	monoaromatics %	diaromatics %	polyaromatics %
Fuel 1	69.8 ± 0.7	27.9 ± 1.0	1.7 ± 0.4	0.6 ± 1.3
Fuel 2	67.6 ± 0.4	28.7 ± 0.5	2.4 ± 0.1	1.4 ± 0.7
Fuel 3	65.8 ± 0.5	30.9 ± 0.5	2.6 ± 0.3	0.6 ± 0.7
Fuel 4	69.5 ± 0.8	19.1 ± 0.4	9.5 ± 0.1	1.9 ± 1.3
Fuel 5	90.5 ± 1.2	4.6 ± 1.4	3.7 ± 0.5	1.2 ± 3.0
Fuel 6	64.9 ± 0.2	31.2 ± 0.4	2.9 ± 0.2	0.9 ± 0.4
Fuel 7	64.6 ± 0.3	32.6 ± 0.3	2.7 ± 0.1	0.2 ± 0.2
Fuel 8	69.0 ± 1.2	24.6 ± 1.4	5.8 ± 0.6	0.6 ± 2.0
Fuel 9	72.6 ± 1.9	20.7 ± 2.3	6.0 ± 0.3	0.7 ± 4.1
Fuel 10	63.6 ± 0.2	33.1 ± 0.2	3.0 ± 0.2	0.4 ± 0.2
Fuel 11	67.2 ± 0.5	30.1 ± 0.4	2.5 ± 0.2	0.3 ± 0.6
Fuel 12	65.8 ± 0.4	31.6 ± 0.1	2.1 ± 0.2	0.5 ± 0.4
Fuel 13	67.0 ± 0.1	29.6 ± 0.2	2.9 ± 0.2	0.4 ± 0.2

Table 4. Absolute Error between SFC and GC-Vacuum UV Determinations of Diesel and LGO Sample Using Dynamic Spectral Filtering

SFC vs vacuum UV	saturates %	monoaromatics %	diaromatics %	polyaromatics %
Fuel 1	−0.1	−0.7	1.7	0.6
Fuel 2	−1.8	−0.6	1.0	1.4
Fuel 3	12.6	2.8	−14.5	−1.0
Fuel 4	4.8	−9.5	3.4	1.3
Fuel 5	−4.1	−0.2	3.1	1.2
Fuel 6	−1.1	−0.4	0.5	0.9
Fuel 7	0.0	0.2	−0.3	0.2
Fuel 8	3.4	−2.3	−1.0	−0.2
Fuel 9	1.7	−4.5	2.0	0.7
Fuel 10	1.0	−1.3	0.0	0.4
Fuel 11	0.1	−0.8	0.5	0.3
Fuel 12	−1.2	0.2	0.5	0.5
Fuel 13	−4.8	12.1	−7.8	0.4

docosane peak around 4 min in red; the blue trace (aromatic) shows no significant response to this analyte. This is a general property exhibited by saturates and aromatics, allowing these classes to be distinguished based on appropriately filtered chromatograms. However, while saturates do not contribute significantly to the "aromatics" filter, all of the compounds in the standard mix contribute to the "saturates" filter, since the aromatic compounds still absorb weakly in the "saturates" region (Figure 1). This will be addressed later when detailing quantitative aspects of the method.

With real diesel samples (Synfuel samples), the GC method with a start temperature of 120 °C (Method 1) was not suitable. This was due to the rapid elution of a significant mass of saturates at the beginning of the chromatogram. Figure 3B shows the vacuum UV absorbance spectrum collected at 2.2 min of the chromatogram in Figure 3A. The 125−160 nm region of the absorbance spectrum exhibits a noisy plateau at an intensity of 2−4 absorbance units (1.0−0.01% T). At this absorbance, the light incident on the detector is too dim to be accurately recorded, resulting in saturation of the absorbance signal at $\lambda < \sim 145$ nm in the early region of the chromatogram.

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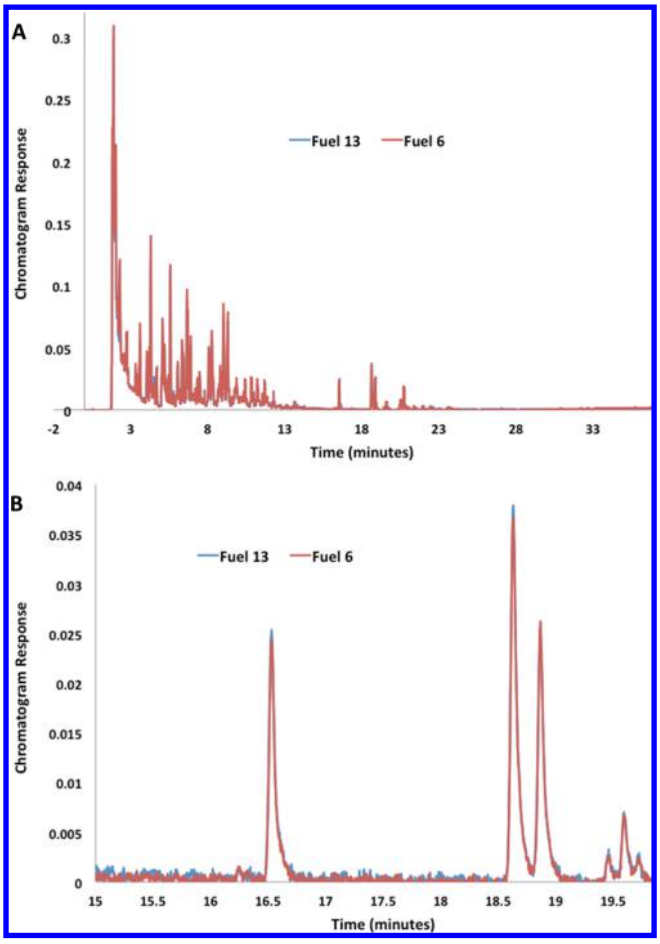

Figure 5. Overlay of GC-vacuum UV results for Fuel 6 and Fuel 13. (A) Full overlaid chromatograms and (B) expanded region between 15 and 20 min. SFC results for these two fuels indicated significant differences in their composition. GC-vacuum UV shows that the fuels are essentially identical.

Table 5. Comparison of Vacuum UV and SFC Data for Samples Fuel 6 and Fuel 13

	saturate %	monoaromatic %	diaromatic %	polyaromatic %
SFC Fuel 6	66.0	31.6	2.4	0
vacuum UV Fuel 6	64.9	31.2	2.9	0.9
SFC Fuel 13	71.8	17.5	10.7	0.0
vacuum UV Fuel 13	67.0	29.6	2.9	0.4

Thus, the separation had to be modified to account for detector response. Method 2 was implemented wherein the initial temperature was decreased to 60 °C and held for 3 min before being increased linearly at 20 °C min^{-1} to 210 °C. Method 2 successfully spread the initial mass of hydrocarbons out across a broad enough timespan that detector saturation was avoided. It is worth noting that (a) even though Method 1 is referred to as the "FID-optimized" method, due to the lack of a selective response, an FID would not have been suitable for quantification in either method due to the saturate/monoaromatic coelution, and (b) if a larger vacuum UV dynamic range were desired, the saturate response could in principle have been based on the use of multiple spectral

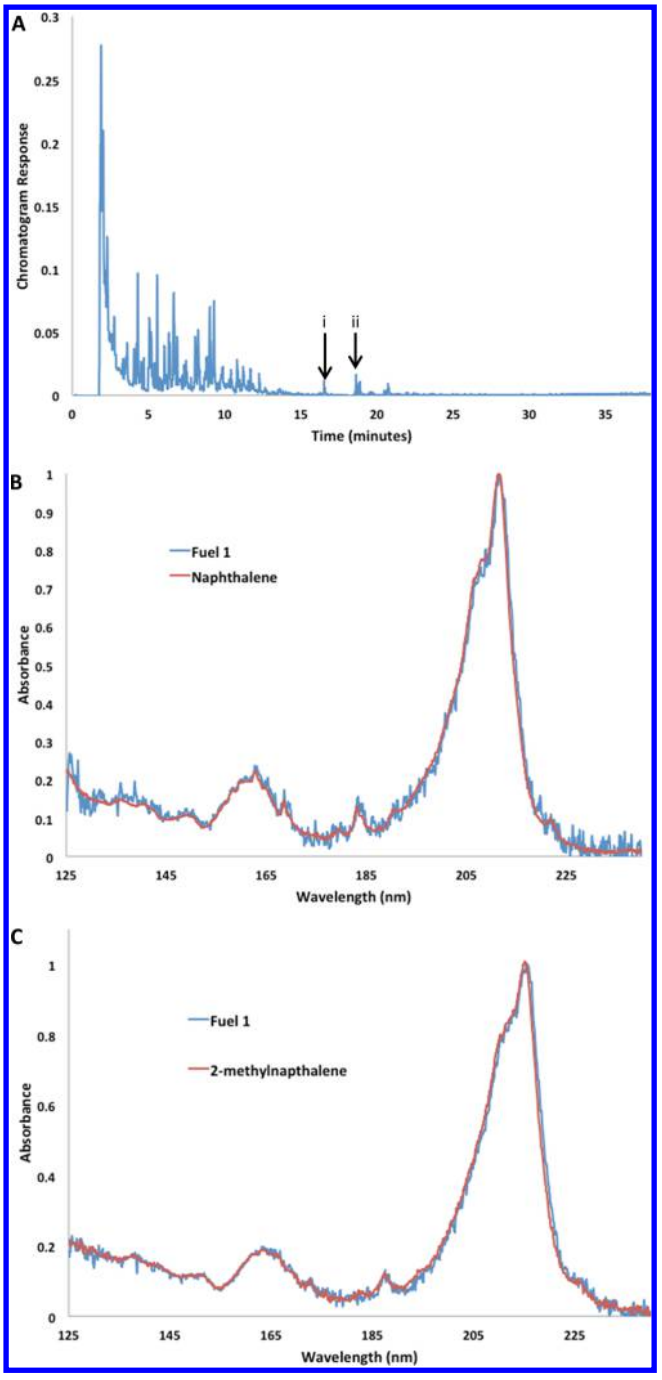

Figure 6. GC-vacuum UV results for the analysis of Fuel 1. SFC data indicated 0 diaromatic content. Vacuum UV clearly indicates presence of diaromatics. (A) Chromatographic data, full-range filter (average absorbance over 120 nm < λ < 240 nm). (B) Background-corrected absorbance spectrum collected at (i) ~16.5 min (blue), matched with library spectrum for naphthalene (red). C) Background-corrected absorbance spectrum collected at (ii) ~18.7 min (blue), matched with library spectrum for 2-methylnaphthalene (red).

windows for quantification (e.g., 125−140 nm for low abundance compounds and 145−160 nm for higher abundance compounds, with corresponding relative response factors). This latter approach was not used in this research and is only mentioned to indicate the possibility.

Method 2 was then used to test a series of Synfuel samples, and the regions of the chromatogram corresponding to each

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Table 6. Comparison of Vacuum UV and SFC Data for QC Sample ± Standard Deviation[a]

	saturate %	monoaromatic %	diaromatic %	polyaromatic %
SFC-QC	66.6 ± 0.4	31.3 ± 0.4	2.1 ± 0.1	0
vacuum UV-QC	66.5 ± 0.2	31.2 ± 0.1	2.6 ± 0.0	0 ± 0.2

[a] n = 3 for GC-vacuum UV.

group type were determined. The start of the diaromatic region and end of the monoaromatic/saturate region is indicated by the start of the naphthalene peak, while the end of the diaromatic region is marked by the start of the anthracene peak, which also marks the beginning of the polyaromatic region. These peaks can be easily identified using the corresponding vacuum UV absorbance spectra, as illustrated in Figure 4. In the chromatographic domain (Figure 4, top), the peak of interest is selected (i) as well as a background region (ii). The average, experimental, background-corrected absorbance spectrum of the peak is then reported (Figure 4, bottom). In this case, the peak (naphthalene) marks the division between the [monoaromatic (M) + saturate (S)] and diaroamtic (D) regions. This absorbance spectrum is then matched to library spectra to confirm the identity of the compound and the point at which to apportion the signal between groups. The point to split the signal between diaromatic and polyaromatic is identified similarly. Once the regions are selected, the total response areas for each grouping along with the group relative response factors are used to calculate the mass percentages for each group type.

Since a full-range absorbance spectrum is obtained during each detector scan, a chromatographic response can be generated using any number of spectral range filters. These filters are typically the average detector response over a range of wavelengths ($R_{\lambda(j)\text{-}\lambda(k)}$), given by eq 1, where j and k are the indices in the spectral dimension corresponding to the lower and upper bounds on the wavelength range for the filter, respectively, and $A_{\lambda(i)}$ is the absorbance recorded at wavelength i.

$$R_{\lambda(j)-\lambda(k)} = \frac{1}{(k-j)} \times \sum_{i=j}^{k} A_{\lambda(i)} \tag{1}$$

Applying the filter to a chromatogram thus results in a univariate response vector of $R_{\lambda(j)\text{-}\lambda(k)}$ from t = 0 to the end of the chromatogram. Generally the full-range response, $R_{125-240}$ is used to visualize the chromatogram as a whole.

On the basis of the retention times identified by the starts of the naphthalene and anthracene peaks, the $R_{125-240}$ filtered chromatogram is divided into three regions and three total areas based on this filter are calculated. The region of $R_{125-240}$ from t = 0 to the start of the naphthalene peak represents the monoaromatics/saturates response, $AMS_{125-240}$. The region of $R_{125-240}$ between the start of the naphthalene peak and the start of anthracene is the diaromatic response, $AD_{125-240}$, and the region of $R_{125-240}$ from the beginning of the anthracene peak to the end of the chromatogram is the polyaromatic response, $AP_{125-240}$. Here we note that it is permissible to compute a response "area" that simply consists of the summed response over each region, provided the scan rate remains constant. The relationship between this total response and an integrated area is a multiplicative factor (the time between scans) that does not affect any of the determined mass % results reported. If the scan rate were changed midrun, this would not hold true. The response is usually background-corrected by sampling a baseline region just prior to the region of interest.

In the monoaromatic/saturate region, both monoaromatics and saturates contribute to the 125−240 nm response area. However, monoaromatics absorb strongly in the 170−200 nm region while saturated hydrocarbons absorb very little in this region. In fact, a response filter in the 175−205 nm region responds negligibly to saturated hydrocarbons, while still responding strongly to monoaromatics. Thus, a monoaromatic-only response, $AM_{175-205}$, can be determined from the region of $R_{175-205}$ from t = 0 min to the start of naphthalene peak. Further, the full 125−240 nm response for monoaromatics, $AM_{125-240}$, can be predicted from $AM_{175-205}$, based on the relative response for monoaromatics over these two wavelength regions. The saturate-only response over the entire spectral window, $AS_{125-240}$, can then be calculated using eq 2.

$$AS_{125-240} = AMS_{125-240} - AM_{125-240} \tag{2}$$

The relative response for monoaromatics was initially estimated based on the range of petroleum-like monoaromatic spectra in the VUV spectral library, which showed that $AM_{125-240} \approx 0.50 \times AM_{175-205}$. When testing the method with actual diesel samples for which there were reliable historical SFC data, it was found that a factor of 0.5555 rather than 0.50 yielded results that were in better agreement between the two techniques. This is likely due to a larger distribution of monoaromatic species in real diesel samples as compared to monoaromatic spectra currently available in the VUV library.

Once the response areas for all of the compound groups were determined, the mass percent for each group type was calculated according to eqs 3−6:

$$M\% = 100 \times \frac{AM_{125-240} \times RRF_M}{(AM_{125-240} \times RRF_M) + (AD_{125-240} \times RRF_D) + (AP_{125-240} \times RRF_P) + (AS_{125-240} \times RRF_S)} \tag{3}$$

$$D\% = 100 \times \frac{AD_{125-240} \times RRF_D}{(AM_{125-240} \times RRF_M) + (AD_{125-240} \times RRF_D) + (AP_{125-240} \times RRF_P) + (AS_{125-240} \times RRF_S)} \tag{4}$$

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$$P\% = 100 \times \frac{AP_{125-240} \times RRF_P}{(AM_{125-240} \times RRF_M) + (AD_{125-240} \times RRF_D) + (AP_{125-240} \times RRF_P) + (AS_{125-240} \times RRF_S)} \quad (5)$$

$$S\% = 100 \times \frac{AS_{125-240} \times RRF_S}{(AM_{125-240} \times RRF_M) + (AD_{125-240} \times RRF_D) + (AP_{125-240} \times RRF_P) + (AS_{125-240} \times RRF_S)} \quad (6)$$

where RRF is the relative response factor for the corresponding group type: $RRF_M = RRF_D = RRF_P = 0.275$, and $RRF_S = 0.775$. The relative response factors are relative proportionality factors for converting area response to mass and were obtained from VUV Analytics' prior studies of gasoline-range samples for PIONA analyses (manuscript in preparation). In that work, a PIONA standard was used to determine relative response factors for each of the five PIONA (Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics) classes. These class-based relative response factors were adapted and used as a starting point for the present work. The relative response factor for saturates, RRF_S, was set to the average of the paraffin, isoparaffin, and naphthene class relative response factors. The prior PIONA analysis did not determine relative response factors for di- and polyaromatic compounds, and these were set equal to the monoaromatic relative response factor. Note that the class-based RRFs are averages over large numbers of molecules from each class and are more appropriate for bulk composition determinations than for speciation of individual compounds, since the values for individual compounds can vary from these averages. These group-type response factors were tested for this particular application to diesel and light gas oil (LGO) samples.

In comparing the first-pass analysis with the prior SFC results, there were a few samples that stood out with large differences from the SFC results across all sample types and for all the classes. Of these, the monoaromatics class was the worst with an average absolute error of 6%, a minimum of 1% and a maximum of 14% errors. Upon closer inspection, it was noted that the monoaromatic and diaromatic regions were coeluting to varying extents in the samples. Since no attempt had been made to decouple monoaromatic and diaromatic responses when these classes coelute, this overlap resulted in poor determination of the relative amounts of these groups. In order to improve the separation between group types, the oven programming rate was decreased from 20 °C min^{-1} to 5 °C min^{-1}. This solved the coelution issue between monoaromatic and diaromatic groups, resulted in better agreement with the prior SFC results and motivated further development of the method, as described below.

To further validate the method, beyond comparing results with the SFC results, Fuel 7 was randomly chosen from the samples which agreed with the SFC result at the 5 °C/min ramp rate and subjected to standard addition determination. Standard addition was performed by spiking a known weight percent of the group-type of interest into aliquots of Fuel 7 at four different concentrations for each group type, with the range for each group type depending on the solubility of the compounds. The results of the standard addition experiments along with results based on vacuum UV determination using both the 20 °C min^{-1} and 5 °C min^{-1} ramp rates are presented in Table 1. The vacuum UV determination at 5 °C min^{-1} ramp rate and the standard addition determinations yielded results that were in better agreement with the SFC results for this sample.

In an attempt to further improve the aromatic characterization of these samples, a new spectral filtering strategy was devised. The previous results were calculated based on the use of static filters: average area response recorded over a specific, fixed spectral window (e.g., average over 125−240 nm). In order to improve specificity, signal-to-noise, and decrease the influence of fluctuations in the background, a dynamic filtering strategy was explored. With a dynamic filter, a specific region of the spectrum is defined as a *search window*. This is a region where a characteristic strong absorption band is expected for a group of compounds (e.g., 200−240 nm for di- and polyaromatics). The dynamic filter then identifies the wavelength of maximum absorbance within this search window and tracks the average response within a narrow (here ±2 nm) subwindow about the wavelength of maximum absorbance within the search window (e.g., ∼208 ± 2 nm for naphthalene (Figure 1)). The dynamic filter was investigated for determination of the responses in the diaromatic and polyaromatic regions where search windows were defined that would encompass two- or three-ring spectral features. Equations 3−6 were modified accordingly to account for the new filters and relative response factors:

$$M\% = 100 \times \frac{AM_{125-240} \times RRF_M}{(AM_{125-240} \times RRF_M) + (AD_{max,200-240} \times RRF_{D,max}) + (AP_{max,200-240} \times RRF_{P,max}) + (AS_{125-240} \times RRF_S)} \quad (7)$$

$$D\% = 100 \times \frac{AD_{max,200-240} \times RRF_{D,max}}{(AM_{125-240} \times RRF_M) + (AD_{max,200-240} \times RRF_{D,max}) + (AP_{max,200-240} \times RRF_{P,max}) + (AS_{125-240} \times RRF_S)} \quad (8)$$

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Anal. Chem. 2016, 88, 5809−5817

$$P\% = 100 \times \frac{AP_{max,200-240} \times RRF_{P,max}}{(AM_{125-240} \times RRF_M) + (AD_{max,200-240} \times RRF_{D,max}) + (AP_{max,200-240} \times RRF_{P,max}) + (AS_{125-240} \times RRF_S)} \quad (9)$$

$$S\% = 100 \times \frac{AS_{125-240} \times RRF_S}{(AM_{125-240} \times RRF_M) + (AD_{max,200-240} \times RRF_{D,max}) + (AP_{max,200-240} \times RRF_{P,max}) + (AS_{125-240} \times RRF_S)} \quad (10)$$

where $AD_{Max,200-240}$ and $AP_{Max,200-240}$ are the response areas for the diaromatic and polyaromatic regions, respectively, as determined from the dynamic filters. Since the response areas for these two regions are no longer determined from a full-range response, the relative response factors for these groups were replaced with $RRF_{D,Max}$ and $RRF_{P,Max}$ which were determined from the standard addition data and assigned values of 0.045 and 0.09, respectively.

The use of the dynamic filter further improved the agreement of the results with the SFC data as shown in Tables 2, 3, and 4. Table 2 presents the dynamic filtering method applied to Fuel 7, Table 3 shows the results when the method with dynamic filtering and the 5 °C min^{-1} ramp rate was used for the series of diesel and LGO samples. Table 4 shows the absolute differences observed between the dynamic filtering GC-vacuum UV method and SFC results for the same series of diesel and LGO samples.

It is immediately apparent that Fuels 3−5 had the largest errors between GC-vacuum UV and SFC results. This is not surprising as these were LGO samples with a slightly heavier distribution of compounds than diesel. While we do not have the original SFC data (this experiment was outsourced by our industry partner previous to the present work), it was collected according to CAN/CGSB-3.0 No. 15.0-94, a method which is historically suspect for LGO samples due to the fact that baseline resolution between group types was not always achieved, according to our industrial partner. Careful inspection of the results for these samples showed that for the GC-vacuum UV method there were no coelutions between monoaromatics and diaromatics and that the only coelutions observed were ones that could be resolved in the spectral domain, monoaromatic/saturate and diaromatic/polyaromatic.

Of the diesel samples, Fuels 1, 6, and 13 were examined closely. For Fuel 13, the SFC results were nonsensical in light of the vacuum UV results. A comparison of the chromatogram for Fuel 13 with Fuel 6 (Figure 5) showed that the two fuels were nearly identical. Comparing the quantitative results for these two fuels (Table 5) shows that the two fuels are indeed very similar according to vacuum UV, though the results from SFC suggest marked differences between the fuels. Here, the vacuum UV result is arguably more reliable due to the added information provided in the spectral domain and is consistent with the observed chromatographic data.

Errors in the diaromatic content were noted for Fuel 1 where according to the SFC results, there was no diaromatic content; however, as shown by GC-vacuum UV (Figure 6) there is obvious diaromatic content (naphthalene and 2-methylnaphthalene peaks are confirmed based on retention times and vacuum UV absorption spectra). This points to the utility of the spectral dimension of the data for obtaining reliable results.

A current challenge for the vacuum UV measurement are the relatively large errors for the polyaromatic region in this data set (generally 1−2%). These errors are attributed to a combination of the relatively low abundance of polyaromatics in these samples combined with the baseline variation that was observed over the polyaromatics region. The analysis of samples with higher polyaromatic content combined with new baseline tracking and subtraction routines (currently in development by the vendor) should improve the performance of the method for polyaromatic content determination. It is worth noting that while the polyaromatic errors are large compared to the errors for the other groups (Table 3), the polyaromatic errors are generally in the range of 1−2%, reaching a maximum for one sample of 4%.

As a further test of the new method, a Syncrude quality control sample (well characterized diesel) was measured. SFC data had been collected for this sample from 2010−2012. A comparison of the SFC and vacuum UV method results for this sample are presented in Table 6. The two techniques agree with each other within the error estimates, providing further evidence that the new vacuum UV method is capable of providing group-type composition results for diesel fuels.

CONCLUSIONS

A GC-vacuum UV method was developed to perform mass percent quantification and group-type separations of diesel range petroleum samples including light gas oils. The method was generally in agreement with SFC data for the samples collected in accordance with the ASTM D5186 and CAN/CGSB-3.0 No. 15.0-94 methods. Where the two methods did not agree, it was shown that the vacuum UV results were more defensible due to the spectral dimension of the data which could provide qualitative information for identification and improved selectivity between group types.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.6b00383.

Table S1, difference in mass % of different compound groups in diesel samples determined using SFC and GC-VUV Method 2 (PDF)

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Notes

The authors declare no competing financial interest.

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