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Quantitative analysis of hydrocarbons in Gas oils by Two-dimensional Comprehensive Gas Chromatography with Vacuum Ultraviolet Detection

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Abstract

Gas oils (GOs) analysis is essential for production process control, in order to meet quality standards, render these products safer for the environment and support research for alternative fuels. GOs quantitative analysis can be commonly achieved by employing two-dimensional comprehensive gas chromatography with flame ionisation detection (GC×GC/FID) in combination with identification templates. However, in order to perform quantification for families which coelute in GC×GC analysis (e.g. olefins/naphthenes or monoaromatics/polynaphthenes) prefractionation of gas oil before GC×GC analysis is necessary. Recent introduction of the Vacuum ultraviolet (VUV) detector has offered new possibilities in GOs analysis, as this detector can discern between the majority of hydrocarbon families thus possibly rendering the gas oil prefractionation unnecessary. Additionally, it can perform quantification according to Beer-Lambert's law provided that VUV relative response factors (RRFs) are known. The purpose of this work is to report, for the first time, VUV RRFs for numerous hydrocarbons according to their family and their carbon number (ca. 160) in GOs, permitting

to perform direct quantification of hydrocarbons in GOs without prefractionation. VUV RRFs were measured by using a GC×GC-VUV/FID dual detection set-up in which FID was employed as a quantitative reference. In order to obtain VUV RRFs representative for any gas oil, a set of 14 GOs with different origins was employed. Both VUV RRFs averaged in 125-240 nm range and spectral VUV RRFs (reference spectra) were obtained. It was demonstrated that VUV RRFs were similar between employed GOs allowing their universal use. Obtained RRFs were used to perform hydrocarbons quantification for a light cycle oil (LCO) by GC×GC/VUV, with olefins and naphthenes being quantified through spectral decomposition. Good comparability with results obtained by prefractionation was observed demonstrating the great interest of the GC×GC/VUV approach for the detailed and rapid analysis of hydrocarbons in gas oils.

1. Introduction

Quantification of hydrocarbons present in GOs can be achieved by using GC×GC coupled with FID detection [1–7]. FID exhibits excellent quantitative performance for C containing compounds however it provides minimal qualitative information. To circumvent this issue, GC×GC identification templates are designed depending on the selected GC×GC column set. Template zones typically contain groups of constitutional isomers having the same carbon number and similar polarity, in accordance with the roof-tile effect [8]. This approach is fully adapted for quantification of families which do not coelute in GC×GC analysis. However, as FID does not provide qualitative information, it cannot properly handle coeluting species that cannot be discriminated by GC×GC analysis. For gas oils, these species are mainly olefins and diolefins that coelute with naphthenes, but also polycyclic naphthenes that are eluted with monoaromatics. These compounds are not resolved whatever the GC×GC configuration employed (normal *i.e.* $^{1D}\text{non polar} \times ^{2D}\text{polar}$, or reverse configuration *i.e.* $^{1D}\text{polar} \times ^{2D}\text{non polar}$).

In order to circumvent the mentioned issue, one option is to prefractionate each investigated sample prior to GC×GC analysis. For this purpose, as proposed in the literature, preparative LC [9,10], solid phase extraction SPE [11] or online supercritical fluid chromatography SFC [12] can be used. These techniques have demonstrated good capabilities in separating saturated compounds from non-saturated ones, including olefins. But they remain tedious, costly and time-consuming and therefore are hardly compatible with intensive routine laboratory analysis.

Contrary to FID, mass spectrometry (MS) offers selectivity for hydrocarbon families as detected ions are different from one family to another. Hyphenation of MS with GC×GC for the quantitative analysis of hydrocarbons in oil-derived products has thus been extensively studied [13–19]. In these works, electronic ionisation is the most commonly used ionisation mode, soft ionisation source also being employed in some cases [20]. In this field, work of

Jennerwein et al. [14] has shown that proper automated identification may be obtained from GC×GC/MS thanks to adequate Visual Basic scripts that take into account specific m/z fragments for a given family. Making this method quantitative required a complex method to determine MS response factors based on the analysis of numerous standards. The obtained response factors may vary from one instrument to another and MS instruments are generally considered as sensitive instruments that require frequent calibration. That is why most of current GC×GC/MS methods are only semi-quantitative [18] and do not account for response differences between compounds. Finally, MS still fails in discerning compounds that give same fragments and elute in the same region of the 2D chromatographic space such as for example naphthenes and olefins.

Newly introduced vacuum ultraviolet (VUV) broad band absorbance detector has recently attracted a lot of attention. Its amenability for oil and gas characterization has already been demonstrated in a number of works [21–26]. VUV detector possesses the ability to differentiate between different types of compounds based on their spectral signatures, provided that they are sufficiently different [22,27,28]. Additionally, VUV has quantitative abilities according to Beer-Lambert's law, hence it also enables compounds quantification. However, quantification with VUV is not completely straightforward, as different compounds can exhibit various VUV responses. For example, same mass of aromatic species absorbs about 3 times more (depending on the species) in the 125-240 nm range when compared to saturated ones [21]. Hence, compound response needs to be corrected by using appurtenant VUV relative response factors (RRFs).

VUV RRFs have been reported in several works [21,24,29]. Walsh et al. [21] demonstrated RRFs for the purpose of bulk characterization of gasoline samples (PIONA type analysis). Weber et al. [24] achieved mass percent quantification of saturates, mono, di, and polyaromatics

94 in diesel samples. García-Cicourel and Janssen [29] introduced a GC/VUV method for the
95 measurement of the total level of aromatic hydrocarbons in purified mineral oils.

96 VUV has only recently been hyphenated with GC×GC analysis [30–34]. Wang et al. [33] have
97 demonstrated how an additional dimension of separation provided by VUV in GC×GC/VUV
98 analysis can allow to resolve coelution of molecules commonly present in diesel samples.
99 However, the possibility of full quantification of all hydrocarbon families in more complex
100 samples such as gas oils by using VUV RRFs has not yet been reported. This approach would
101 allow to eliminate the need for prefractionation step commonly employed when using
102 GC×GC/FID for GO quantification and render the analysis less time consuming and less costly.

103 The purpose of the present work is to report, for the first time, VUV RRFs for ca. 160 blocks
104 of hydrocarbons in gas oils according to their carbon number. Having such a database of
105 VUV RRFs has permitted to perform direct quantification of hydrocarbons in GOs by
106 GC×GC/VUV without necessity of prefractionation.

107 Methodology for deriving VUV RRFs involved using a GC×GC-VUV/FID dual detection set-
108 up in which FID was employed as a quantitative reference. In order to obtain VUV RRFs
109 representative for any gas oil, a set of 14 GOs with different origins was employed. To obtain
110 RRFs for hydrocarbon families which coelute in GC×GC analysis (namely olefins/naphthenes),
111 all GOs were prefractionated into saturated and unsaturated fractions by using solid phase
112 extraction on silver modified silica. All fractions and nonfractionated GOs were then analysed
113 by GC×GC-VUV/FID and both VUV RRFs averaged for 125-240 nm range and spectral
114 VUV RRFs (reference spectra per unit mass) were derived. Obtained VUV RRFs were then
115 employed to perform quantification for an LCO type gas oil with a GC×GC/VUV instrumental
116 set-up. Olefins and naphthenes were quantified through spectral decomposition and quantitative

117 results obtained by GC×GC/VUV were compared with the one obtained by using GC×GC/FID
118 with prefractionation.

119 2. Materials and methods

120
121 Gas oil database employed for this study was composed of 14 samples from different origins,
122 including 1 straight-run gas oil from atmospheric distillation of crude oils (SR), 3 Light Cycle
123 Oils (LCO) from fluid catalytic cracking units, 4 coker gas oils (GOCK), 2 hydroconverted gas
124 oils (HDCGO) and 4 hydrotreated gas oils (HDT). LCOs and coker gas oils are known to
125 contain large amounts of olefins and diolefins. Gas oils were diluted in n-heptane and toluene
126 before being analysed with GC×GC-VUV/FID or GC×GC/VUV. Gas oil samples were
127 provided by IFP Energies nouvelles.

128 Prefractionation of the gas oils was performed with a preparative LC PuriFlash instrument
129 (Interchim, France), equipped with online UV detector. The following wavelengths were
130 monitored continuously: 200, 254, and 299 nm. Stationary phase consisted of 25 g of silica
131 Davisil 923 (pre-packed cartridge PF-SILICA GEL DAVISON 923-F0025, Interchim, France)
132 + 7 g of silica impregnated with silver nitrate at 10 m/m% (Sigma-Aldrich), divided into two
133 cartridges of 3ml—prepared by hand and connected in series. Gas oil samples were diluted to 10
134 m/m% in n-heptane. 5 ml of the sample solution were injected (around 0.5 g of sample on
135 column). Sample elution was performed in the following order: column conditioning with n-
136 heptane (40 ml/min, t = 2 min), elution with n-heptane (40 ml/min, t = 0-1:45 min) and then
137 with CH₂Cl₂/MeOH 9:1 v/v mixture (40 ml/min, t = 1:45-6 min). Collection of fraction
138 containing saturates was t = 0-1:45 min; and for the fraction containing unsaturates t = 1:45-6
139 min. Fractions were evaporated to few ml by gentle evaporation before GC×GC analysis.
140 Additional details about this procedure are given in Supporting Information.

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3 141 For GC×GC-VUV/FID experiments Agilent 7890A gas chromatograph under hydrogen as
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5 142 carrier gas equipped with a G3486A CFT forward fill/flush differential flow modulator was
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7 143 employed (Agilent Technologies, Inc.). A normal configuration column set was chosen: DB-1
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9 144 column (100% dimethyl polysiloxane; 20 m, 0.1 mm ID, 0.4 μ m; Agilent Technologies, Inc.)
10
11 145 was used in first dimension whereas BPX-50 (50% Phenyl Polysilphenylene-siloxane, 3.2 m,
12
13 146 0.25 mm ID, 0.25 μ m; SGE Analytical Science) was used in the second dimension. Split
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15 147 injections were performed with a temperature programmed Agilent MMI inlet (1 μ L injected,
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17 148 150:1 split ratio). Flow rates in the first and the second dimension were set to 0.15 ml/min (inlet
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19 149 pressure 26.86 psig, average velocity 14.5 cm/s) and 25 ml/min (modulator pressure 13.94 psig,
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21 150 average velocity 605.6 cm/s), respectively. Oven temperature program was 50 °C (3 min) to
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23 151 325 °C at 2.5 °C/min. Modulation period was set to 4.5 s while modulation injection time was
24
25 152 set to 0.18 s, latter was optimised according to [35]. The splitting of the effluent at the outlet of
26
27 153 the second column to VUV and FID was performed with an SGE SilFlow™ GC three port
28
29 154 splitter. Fused silica restrictors (Agilent Technologies, Inc.) were used to direct the flows from
30
31 155 the splitter to the two detectors. Their dimensions were chosen so as to direct about 75 to 80%
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33 156 of the 2D flow to the VUV detector and the remainder of the flow to the FID (determined by
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35 157 the measurement of mass flows at FID and VUV exits). VGA-101 (VUV Analytics, Inc.,
36
37 158 Austin, TX, United States) detector was employed. VUV conditions were as follows:
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39 159 wavelength range, 125–240 nm; acquisition frequency, 50 Hz; flow cell and transfer line
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41 160 temperature 325 °C, make-up gas pressure 0.35 psig. FID conditions were as follows: 325 °C,
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43 161 air flow 400 ml/min, hydrogen 35 ml/min and make-up gas (nitrogen) 25 ml/min, acquisition
44
45 162 frequency 100 Hz.
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54 163 GC×GC with single detection (FID or VUV) for final validation involved the same column set
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56 164 as in GC×GC-VUV/FID method. Same injection conditions and oven programming were
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58 165 employed, while constant flow: 0.15 ml/min (inlet pressure 21.95 psig, average velocity 17.1
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60

cm/s) in first dimension and 10 ml/min (modulator pressure 6.7 psig, average velocity 296.3 cm/s) in the second dimension were applied. In the case of the GC×GC/FID / GC×GC/VUV configuration, lower 2D flow was applied due lower pressure drop as no splitter or restrictor was used. Modulation period was 4.5 s and injection time of the modulator 0.18 s for GC×GC/FID analysis and 0.22 s GC×GC/VUV analysis. Difference in flow modulator injection times for GC×GC/FID and GC×GC/VUV analysis comes from the fact that VUV features additional transfer line and flow cell under constant high temperature, this additional pressure resistance decreases effective flow in the second dimension, hence for GC×GC/VUV higher modulation injection time had to be employed in order to ensure complete flushing of the modulation channel. VUV conditions were the same as for GC×GC-VUV/FID analysis. FID detection conditions were 325 °C, air flow 350 ml/min, hydrogen 20 ml/min and make-up gas (nitrogen) 25 ml/min, acquisition frequency 100 Hz.

Agilent ChemStation B.04.03-SP1 was used for GC method control and FID data acquisition. VUVision™ 3.0.1 software was used for VUV data acquisition. Plug im! software [36] was employed for GC×GC data visualization, baseline and noise correction and spectra extraction from individual template zones. Parameters for data pre-processing used in this work are available in ref [37]. 2DChrom v3.1.0 in-house software was employed for GC×GC chromatogram integration. Template alignment was performed with in-house software “Déformation de masque pour la GC×GC v1.50” partly based on the methodology described in [38].

3. Results and discussion

3.1. Methodology for determining VUV RRFs for hydrocarbons in gas oils

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3 190 Evaluating VUV RRFs and VUV reference spectra traditionally requires the injection of
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5 191 standards to record their spectral response. However, for gas oil samples, this approach is not
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8 192 easily applicable due to sample complexity, as there is a limited availability of commercial
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10 193 standards for hydrocarbons contained in gas oils. An alternative approach consists of building
11
12 194 a sample set of representative gas oils and using them to determine mean VUV reference spectra
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14 195 for lumps of isomers (clusters of structural isomers having the same molecular formula) that
15
16 196 are usually separated by GC×GC analysis. A mandatory requirement is that coelutions must be
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19 197 avoided in order to determine pure reference spectra.
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22 198 Hence, a sample set of 14 gas oils from different sources (refinery streams, gas oil from
23
24 199 atmospheric distillation of crude oil) was constructed. To limit coelutions for the determination
25
26 200 of VUV RRFs, all gas oils were first prefractionated into a saturated and an unsaturated fraction
27
28 201 by solid phase extraction on a silver-impregnated silica gel. Each fraction was then analysed
29
30 202 with GC×GC-VUV/FID with dual detection in split mode. Obtained signal was subjected to
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32
33 203 pre-processing, which involved noise reduction, baseline correction and detector blank
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35 204 subtraction. Subsequently, identification templates were applied on all chromatograms
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37 205 (14 saturated, 14 unsaturated fractions and 14 nonfractionated gas oils). Then, calculation of
38
39 206 VUV RRFs was performed, where FID was employed as a quantitative reference allowing to
40
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42 207 scale VUV responses to unitary mass. This strategy is summarized in Figure 1.
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46 208 **3.2. Gas oil prefractionation**

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49 209 Prefractionation method was devised by conducting a separate study involving a model mixture
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51 210 containing selected saturated and unsaturated hydrocarbon species. Test mix composition is
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53 211 given in the Table S1 in the Supporting Information. Figure S1B illustrates generated elution
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56 212 profile for the employed model mixture which demonstrates efficient separation of the two
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groups of interest, namely saturated and unsaturated species. After validation on a test mixture, method was applied to the fractionation of 14 GOs samples contained in the sample set.

3.3. Noise reduction and baseline correction for VUV data

VUV chromatograms for 14 investigated GOs and their fractions were acquired in the 125-240 nm wavelength range. Inherently, VUV chromatograms obtained at high frequencies necessary for GC×GC analysis are quite noisy. The use of fluidic modulation, which involves high flows in the 2D column, additionally decreases VUV signal to noise ratio, thus noise reduction is necessary. Baseline correction is also essential as baseline drift is inherent to GC×GC analysis. As VUV generates multichannel data, for reliable VUV spectra reconstruction it is important that the approach used for both noise reduction and baseline correction is fast, robust and adaptive for each of the wavelengths at which chromatogram is acquired.

Baseline correction of the chromatograms was performed by using a dedicated method based on morphological approach which is an improved version of the method originally proposed in [39]. The approach is based on the estimation of a lower envelope of the observed signal which can be regarded as insertion of segments of finite length below the curve and retaining the envelope produced by all the segments. This can be drastically improved in case of strong noise by calculating the lower envelope from a signal modified by low-pass filter. Considering s the observed signal, f a low pass filter, and B baseline correction from [39], the corrected signal s^* is obtained by $s^* = s - B(f(s))$. Noise correction was performed primarily, based on observation that VUV spectra ought to possess monotonous nature, by choosing an averaging window (number of signal points) for which mean value of the signal will be repeatedly calculated until the entire 125-240 nm range is covered. Additionally to noise and baseline correction, VUV signal demonstrated a detector blank signal which was characterised by higher noise at short wavelengths (close to 125 nm) and long ones (close to 240 nm), which caused artificial

237 deformation of the measured VUV spectra. Average contribution of the detector signal was
238 estimated for a chromatogram section where species do not elute (far end of chromatogram
239 where there is only noise) and this contribution was subtracted at every pixel of the
240 chromatogram. Detailed description of all the pre-processing steps along with chosen
241 parameters for data pre-processing used in this work was provided in [37].

242 Illustration of the influence of each one of these pre-processing stages on the measured VUV
243 spectrum is shown in Figure 2. Traced in black is the extracted summed spectrum from the
244 chromatogram zone where olefins and naphthenes coeluted for an LCO type gas oil. This
245 spectrum was rather noisy and additionally its profile did not correspond to the typical spectrum
246 of an olefin or naphthene from the VUV spectral library (see insert in Figure 2). Further, traced
247 in blue is the spectrum obtained after applying noise correction and outlined in red is generated
248 spectrum after both noise and baseline correction were applied. Even after noise and baseline
249 corrections, obtained spectrum demonstrated higher than zero absorbance at wavelengths
250 longer than 220 nm and even a slight increase of absorbance at 240 nm, which is known not to
251 be the case for olefins or naphthenes. After additional detector blank signal subtraction, a
252 satisfactory spectrum was obtained (traced in green).

253 3.4. GC×GC templates application

254 After appropriate chromatogram pre-processing, identification templates were applied on the
255 whole sample set consisting of 14 GOs and their fractions. Figure 3 illustrates VUV
256 chromatograms (125-240 nm Avg. Abs.) for unsaturated and saturated GO fractions with
257 identification templates applied. Templates were designed so as to clearly define zones in which
258 positional isomers with same molecular formula elute. As GC×GC separation was performed
259 with a classical non-polar / medium-polar column set, the separation of hydrocarbons in the 1st
260 dimension was according to increasing carbon number and in the 2nd dimension according to

their polarity. Thus, on the second dimension compounds were distributed according to increasing aromatic character. On the first dimension template covered carbon numbers from C9 to C30. Detailed templates with all molecular formulas corresponding to each template zone are provided in Supporting Information (Figure S4).

Templates needed to be slightly adjusted each time when applied to another sample, but also when transferred from FID to VUV data for the same sample despite the use of the splitter. To facilitate template alignment, automated anchor point estimation by BARCHAN algorithm [38] was applied and very good template alignment result was obtained for template transformation from FID to VUV data. For very dissimilar samples however, additional anchor points had to be applied manually for optimal transformation.

3.5. Calculation of VUV RRFs for template zones

VUV relative response factor for any compound (RRF_{VUV}^i) was defined as a mass relative response factor. It can be perceived as a scalar if it was obtained from the measurement of the average absorbance for a given wavelength range or as a reference VUV spectrum per unit mass of compound i if the absorbance over the entire spectral range was taken into the account. RRF_{VUV}^i defined in this way, is a constant for a given compound and is directly linked to its absorption cross-section. For GC×GC-VUV/FID set-up, VUV RRFs can be obtained by using the following equation:

$$RRF_{VUV}^i = K(T)^i \cdot \frac{Area_{FID}^i}{Area_{FID}^{ref}} \cdot \frac{Area_{VUV}^{ref}}{Area_{VUV}^i} \cdot RRF_{FID}^i \quad (1)$$

with $Area_{FID}^X$ and $Area_{VUV}^X$ representing the measured response areas on the FID and VUV detectors, respectively for compound i or the reference compound ref , RRF_{FID} and RRF_{VUV} relative response factors for the considered analyte and $K(T)^i$ a temperature dependent

correction factor related to flow splitting effects between the two detectors and that can be determined by the analysis of a mixture of linear paraffins. Details of obtaining Equation 1 and calculating temperature dependent correction factor $K(T)^i$ were provided in [40].

RRF_{FID} represents in the same way as RRF_{VUV} a multiplication factor, necessary to convert response area per unit mass of investigated compound into the area per unit mass of the reference compound. It can be calculated as a ratio of the FID mass response coefficient for compound i and FID response coefficient for a reference compound. Response coefficient for FID in turn can be calculated according to different approaches, for example relative to benzene according to ref [41].

VUV RRFs, obtained in the described way depend only on molecules' cross sections and can be used universally. For calculating VUV RRFs, reference compound or blob whose response is taken to 1 by convention was chosen to be C_{17} n-paraffin for the GO saturated fraction and $C_{10}H_{12}$ tetralin peak for the GO unsaturated fraction (Figures 3A and 3B). In order to rescale VUV RRFs relative to the same reference (*i.e.* n- C_{17}), RRFs calculated in the unsaturated fraction relative to $C_{10}H_{12}$ were corrected by using VUV RRF of $C_{10}H_{12}$ in the nonfractionated sample where n- C_{17} was taken as a reference.

Estimation of the RRFs was performed for each template zone with the condition that the measured FID m/m% is higher than 0.5 %. Mean RRF values from the measurements on the 14 saturated and 14 unsaturated fractions of the database were obtained and standard deviations were determined. It was observed that RSDs of the estimated RRFs were the lowest when average absorbance at full wavelength range 125-240 nm was considered, hence for the final VUV RRFs estimation this wavelength range was employed. Table 1 provides the list of mean VUV RRFs for ca. 160 lumps of isomers present in gas oils according to their chemical family and their number of carbon atoms. Comprehensive list of all obtained VUV RRFs along with

appurtenant RSDs for each template zone is provided in the Supporting Information in Tables S2 and S3. It was observed that despite wide variety of analysed samples, VUV RRFs for the same GO template zone were rather comparable, with weighted relative standard deviation of less than 20% and often less than 10%. It can be assumed that this variation was due to small composition variability between GOs, small imperfection of template alignment and limited sensitivity of the VUV. However, these variations were not of strong significance and as such determined VUV RRFs could have been employed universally for the analysis of gas oils from different origins and without further calibration. In Tables S2 and S3 also reported are average VUV RRFs calculated for each hydrocarbon family and pooled RSDs. These values are well in line with VUV RRFs already reported for PIONA type compounds [21].

Figure 4 illustrates calculated VUV RRFs (average for 14 GOs) on the 125-240 spectral range for several hydrocarbon families according to their carbon number. n-paraffins exhibited VUV response factors which were rather constant (around 1.0) in the observed range of the number of carbon atoms, which is in accordance to theory. As aromatic species absorb more VUV light, their response factors were smaller than the one obtained for saturates. Additionally, RRFs for aromatic species demonstrated an increasing trend with the increase of the number of carbon atoms. This was explained by the fact that the response factors calculated in this study were given per unit of mass. When increasing the number of carbon atoms within a given family, alkyl chains are growing while the aromatic core that is the major UV absorbing chromophore remains the same. Hence, molar absorptivity is almost constant (even if some inductive effects can slightly modify the VUV absorbing properties of the aromatic core) whereas the mass absorptivity is decreasing due to the dilution effect of alkyl chains. With the increase of aromatic character and degree of unsaturation for following hydrocarbon families, a decrease of estimated VUV RRFs was also observed, indicating increased VUV absorbance.

3.6. Extraction of reference VUV spectra

GC×GC analysis of gas oils results in certain coelution events no matter the column set employed. Namely, certain template zones in the GC×GC chromatogram contain a mixture of saturated and unsaturated species. For example, all zones with general formula C_nH_{2n} or C_nH_{2n-2} contain mixture of olefins and naphthenes. Blobs with formula C_nH_{2n-6} and C_nH_{2n-8} contain monoaromatics and polynaphthenes which coelute. To discern relative quantities of these species in their mixture, spectral dimension or more specifically reference spectra per unit mass can be employed.

Reference spectra per unit mass were determined in the same way as VUV RRFs, by using the FID response as a quantitative reference, and by making a correction for flow splitting effects. In this way, obtained reference spectra represented, contrary to epsilon (molar absorptivity) in the Beer-Lambert law, not molar relative values but mass relative values. They corresponded to mass attenuation coefficients (which are the molar absorptivity divided by the molecular weight). Reference spectra were determined for a reduced sample set consisting of 7 GOs (LCO and GOCK), chosen as they are expected to contain significant amounts of olefins.

First VUV summed spectra for each template zone were extracted by using Plug im! software [36]. Then, VUV reference spectra per unit mass were calculated for saturated fraction and scaled to n- C_{17} spectra which was chosen as a reference (its max absorbance was set to 1). For unsaturated fraction $C_{10}H_{12}$ tetralin peak was employed as a reference. All spectra from unsaturated fraction were scaled again as tetralin spectrum relative to n- C_{17} was determined through the analysis of unfractionated GO. Then average values for all 7 gas oils were determined.

Figure 5 shows several examples of the obtained spectra, all scaled to n- C_{17} . Figures 5A, 5B and 5C show spectra for n-paraffins, i-paraffins and non-condensed naphthenes according to increasing carbon number. Spectra for saturates were relatively uniform, which was in line with

previous findings [21]. Figure 5D shows reference spectra for olefins with a clear reduction of absorbance per unit mass with increasing carbon number. The same is observed for alkylbenzenes in Figure 5E and naphthalenes in Figure 5F. Shape of the spectra fitted well with the expected features observed for similar compounds in the VUV spectral library. A bathochromic shift of the maximum absorbance as well as an absorbance increase was observed when aromaticity is increasing. On the contrary, naphthenes and paraffins (n- or iso-paraffins) were hardly distinguishable and their separation with the only spectral dimension was not possible. Separating these compounds thus requires a prior satisfactory chromatographic separation. Olefins and naphthenes demonstrated very different VUV spectra, so did polynaphthenes and monoaromatics, and their spectral differences open the way to quantification through spectral decomposition. Importantly, differences between the spectra within the same family of compounds were observed. For example, in the case of the monoaromatics spectra (Figure 5E), significant difference in absorbance per unit mass between individual monoaromatics species was observed. Thus, more accurate quantification result can be obtained if individual VUV RRFs are used when compared to conventional class based approach [21].

3.7. Spectral decomposition: application to naphthenes/olefins quantification

As previously stated, common problem in group type quantification in gas oils is the quantification of coeluting species, such as olefins and naphthenes. VUV reference spectra obtained as previously described can however be employed to derive contribution of each of the two families to their mixture spectra. In the zone where olefins and naphthenes commonly coelute, observed spectrum for the gas oil is indeed a linear combination of two reference spectra, thus it is possible to calculate the proportion of each of the two families (see Supporting Information Section S4 for more details on calculations).

For the determination of the total amount of olefins and naphthenes in the gas oil, a single template zone was constructed by unifying all zones corresponding to molecular formula C_nH_{2n} or C_nH_{2n-2} . (see insert in Figure 6A). Figure 6A shows obtained reference VUV spectra per unit mass. Traced in blue is the reference spectra for naphthenes averaged for 14 saturated gas oil fractions. In red is the reference spectra for olefins averaged for 7 olefin containing gas oils. Shaded zones illustrate obtained standard deviation of the spectra (up to 10%). It can be seen that the variability is the highest for lower wavelengths, however spectra were still very comparable between different gas oils. Calculated VUV RRFs for this zone were 0.7 for olefins and 1.0 for naphthenes.

These spectra can be further employed for estimation of their linear combination in their mixture spectra obtained for the nonfractionated gas oil for the same template zone. Figure 6B shows traced in black measured spectrum for olefin/naphthene zone for a nonfractionated gas oil of LCO type. Calculated contribution of reference olefin (red) and naphthene (blue) spectra correspond to the multiplication of the reference spectrum by the proportion of each species estimated through spectral decomposition. In green is the calculated spectrum which corresponds to 53% contribution of olefin and 47% of naphthene. Good fit was obtained between measured and calculated spectrum.

3.8. Application of VUV RRFs and spectral decomposition for the GC×GC/VUV analysis of gas oils

Example of application of VUV RRFs and spectral decomposition for estimation of total quantity of olefins and naphthenes is given for an LCO type gas oil. Figure 7 shows the comparison of the generated hydrocarbon distribution according to carbon number for an LCO type gas oil by using GC×GC/FID with prefractionation and by using GC×GC/VUV in combination with VUV RRFs. For olefins/naphthenes zone, spectral decomposition was applied first. After having determined the ratio of olefins and naphthenes, a mean VUV RRF

for this zone was calculated (based on their RRF values mentioned above) and applied to estimate quantity of olefins and naphthenes.

Figure 8 shows obtained group type quantification for the same gas oil where quantity of major hydrocarbon families was reported. Very good agreement between VUV data and FID data was obtained with bias lower than 10% (see insert in Figure 8).

Conclusion

The purpose of this work was to report, for the first time, VUV RRFs for all hydrocarbon lumps (ca. 160) in GOs, permitting to perform their direct quantification by using GC×GC/VUV. Both VUV RRFs averaged in 125-240 nm range and spectral VUV RRFs (reference spectra per unit mass) were obtained, thus enabling spectral decomposition for coeluting species. These data were used to quantify hydrocarbons in an LCO gas oil by GC×GC/VUV according to their family and their number of carbons. Good agreement was obtained between the results of GC×GC/VUV quantification and the results of GC×GC/FID with prefractionation which demonstrated the feasibility and the interest of the GC×GC/VUV analysis for quantification of hydrocarbons in GOs.

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List of Figures

Figure 1 Illustration of the methodology for the determination of VUV RRFs for gas oils quantitative analysis.

Figure 2 Extracted summed VUV spectrum for olefins template zone for an LCO type gas oil: spectrum without pre-processing (in black), spectrum with noise reduction (in blue), spectrum with noise and baseline correction (in red) and spectrum with noise, baseline correction and detector blank signal subtraction (in green). Insert: example of the VUV spectrum of an olefin (1-tetradecene) and naphthene (ethylcyclohexane) from VUVision® spectral library.

Figure 3 VUV chromatogram (125-240 nm Avg. Abs.) for A) coker GO unsaturated fraction and B) coker GO saturated fraction. From bottom to top, template contains following families of hydrocarbons: n-C_nH_{2n+2}, i-C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}, C_nH_{2n-18}, C_nH_{2n-20}, C_nH_{2n-22}, C_nH_{2n-24}, C_nH_{2n-26}.

589 Figure 4 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for selected hydrocarbon
590 families.

591 Figure 5 Reference VUV spectra per unit mass (125-240 nm) relative to n-C₁₇H₃₆ for: A) n-
592 paraffins; B) i-paraffins; C) non-condensed naphthenes; D) olefins; E) alkylbenzenes;
593 F) naphthalenes.

594 Figure 6 A) Average reference spectra per unit mass generated for olefins/naphthenes
595 template zone for saturated and unsaturated gas oil fractions, shaded zones illustrate
596 obtained standard deviation; insert: gas oil template zone for olefins and naphthenes
597 spectra extraction and B) Illustration of spectral decomposition for an LCO type gas
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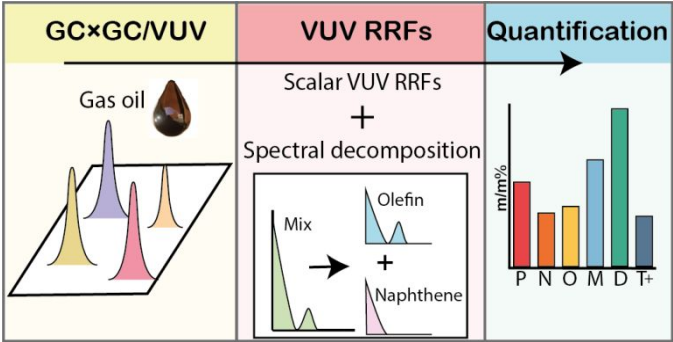
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601 direct quantification result and B) quantification result of the GC×GC/FID
602 with pre-fractionation.

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604 average result for three replicates vs. GC×GC/FID with prefractionation. Insert: parity
605 plot; confidence interval ±10%.

607 List of Tables

608 Table 1 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for saturated and
609 unsaturated gas oil fraction, average values for 14 gas oils are presented.

TOC graphic



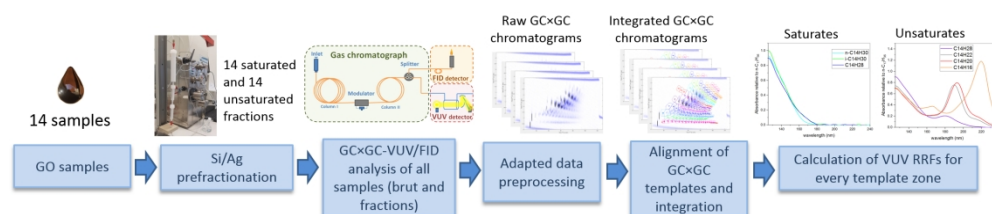


Figure 1 Illustration of the methodology for the determination of VUV RRFs for gas oils quantitative analysis.

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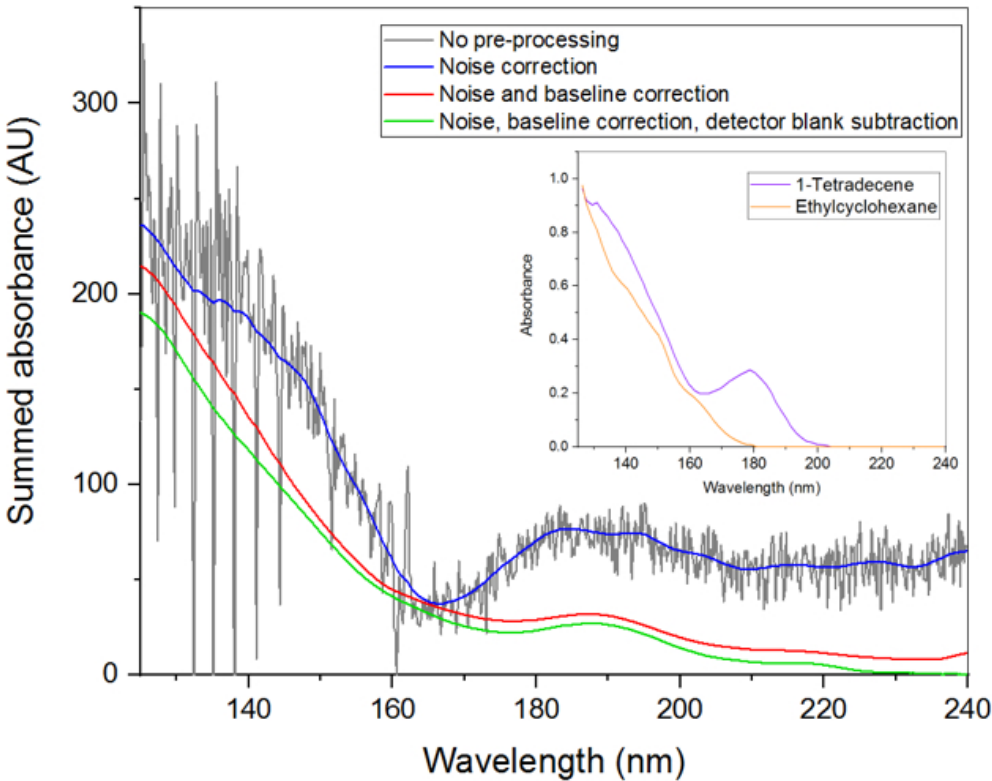


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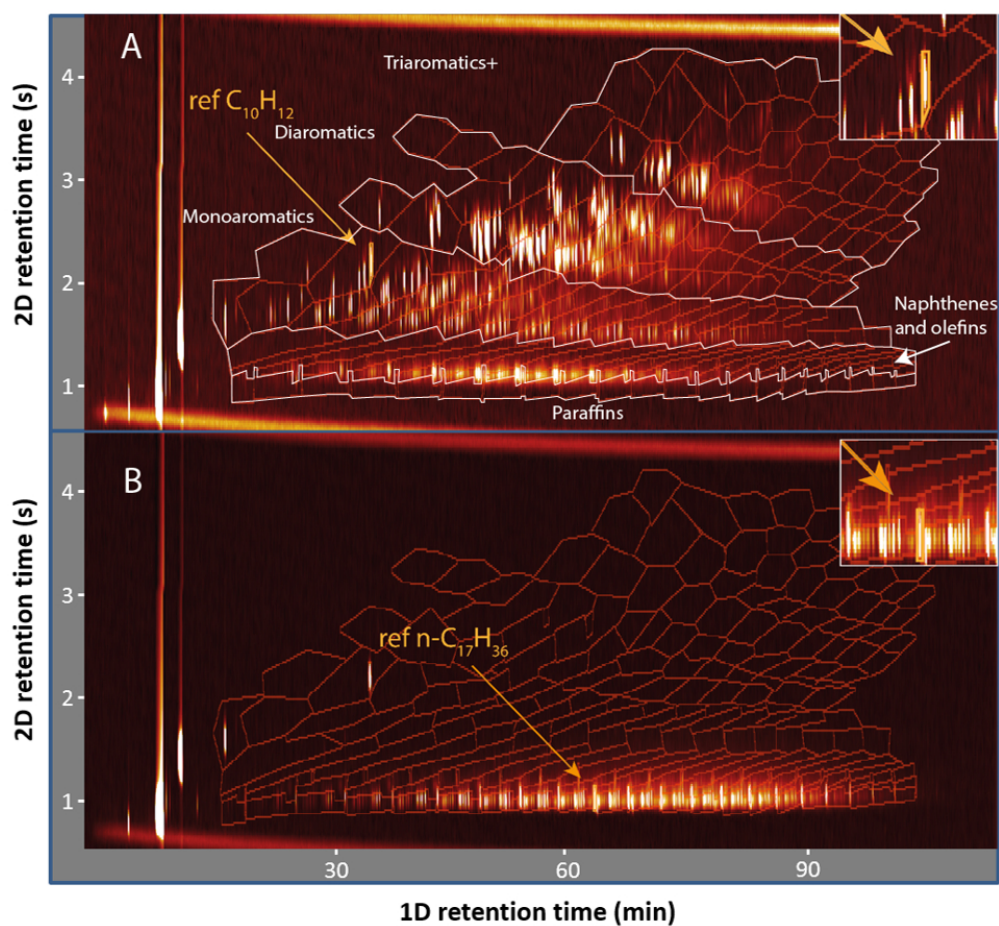


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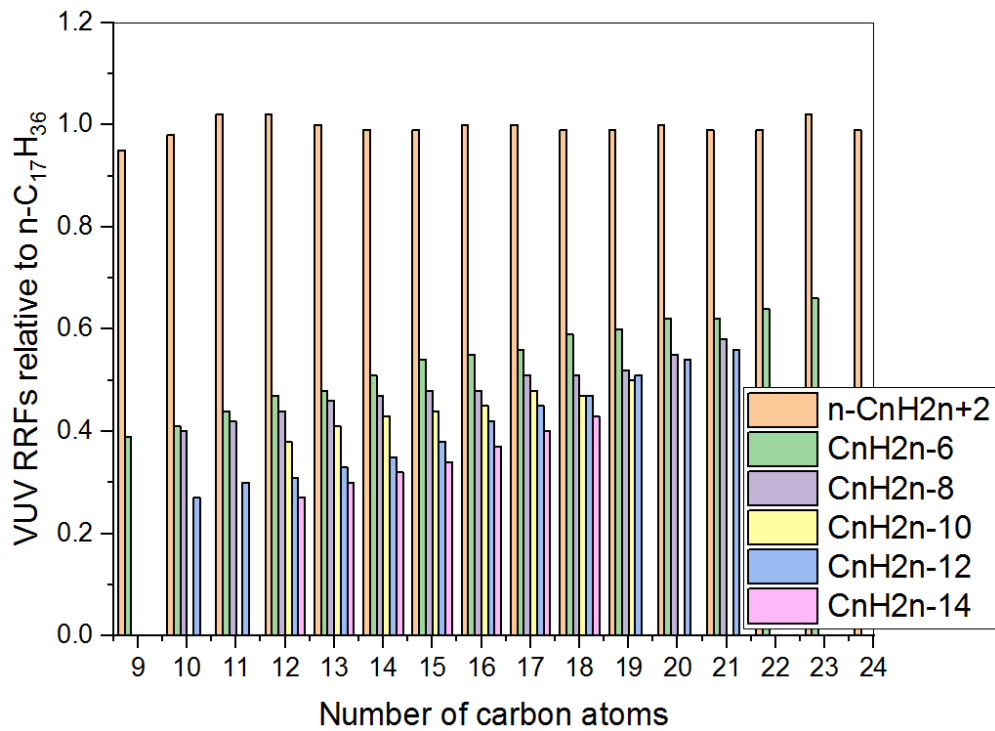


Figure 4 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for selected hydrocarbon families.
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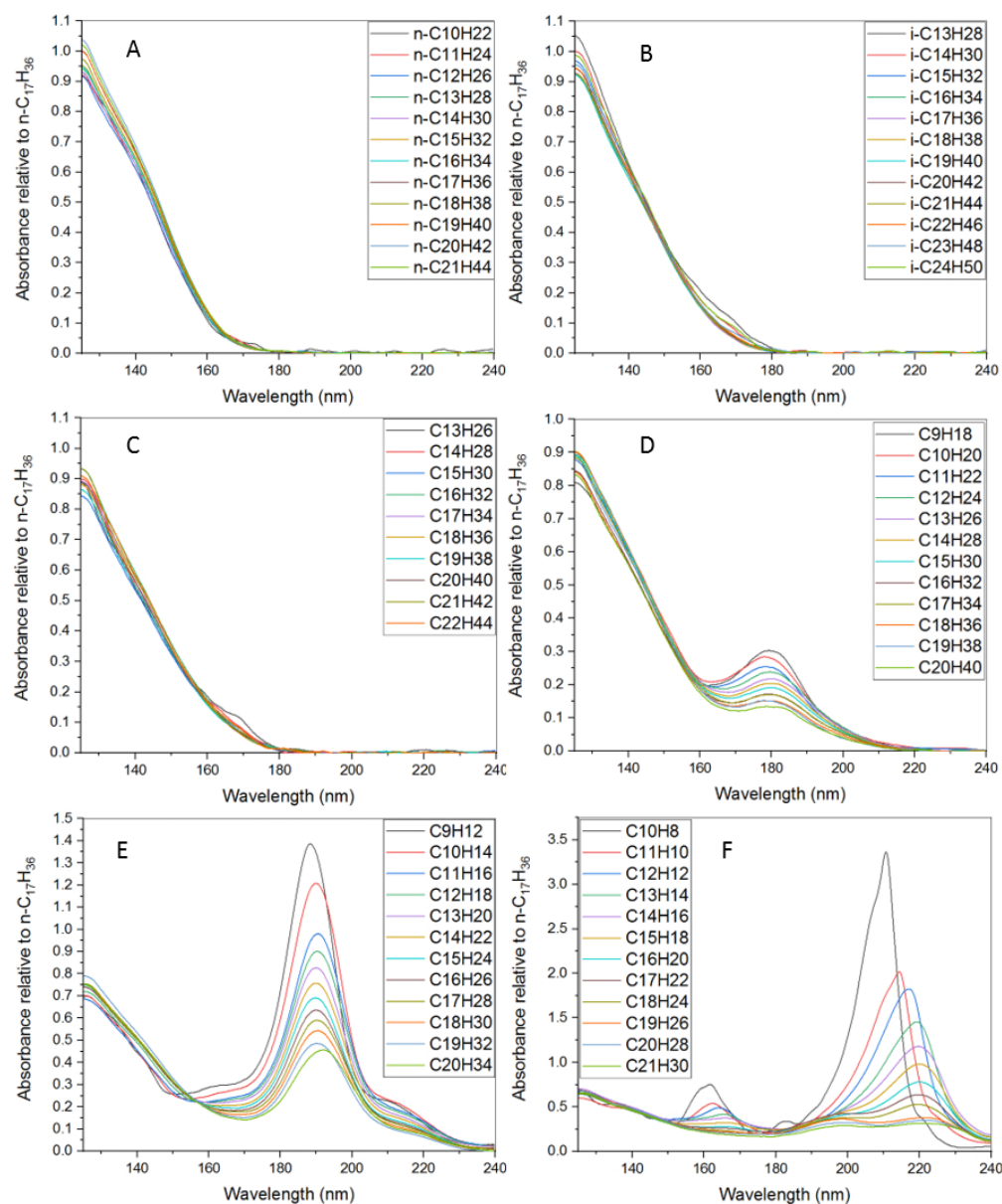


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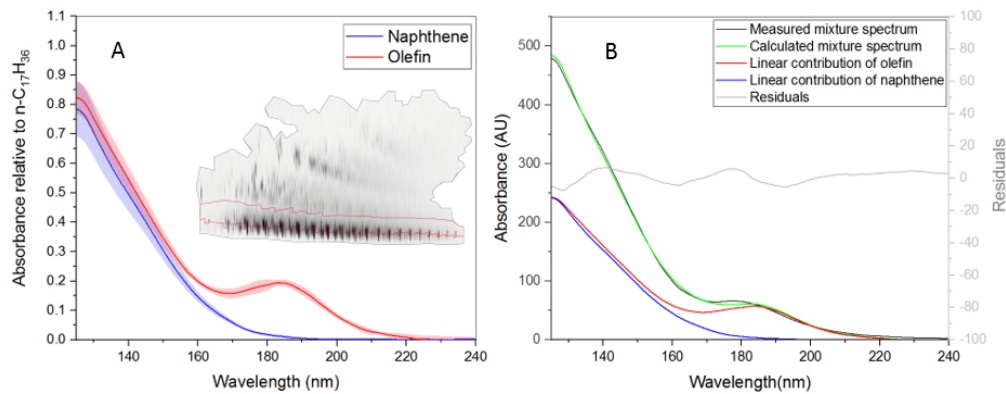


Figure 6 A) Average reference spectra per unit mass generated for olefins/naphthenes template zone for saturated and unsaturated gas oil fractions, shaded zones illustrate obtained standard deviation; insert: gas oil template zone for olefins and naphthenes spectra extraction and B) Illustration of spectral decomposition for an LCO type gas oil, estimated amount of olefin 53 m/m% and naphthene 47 m/m% in the mixture.

78x30mm (300 x 300 DPI)

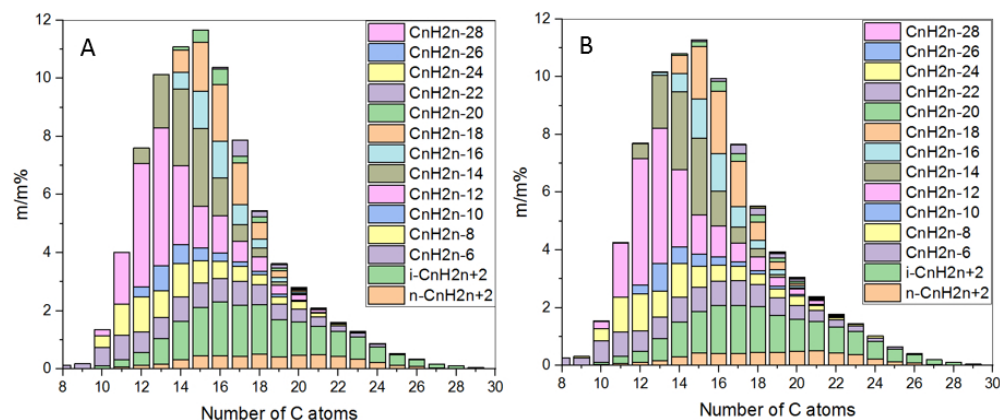


Figure 7 Comparison of the obtained quantification for the hydrocarbon families depending on their carbon number for an LCO type gas oil: A) GCxGC/VUV LCO direct quantification result and B) quantification result of the GCxGC/FID with pre-fractionation.

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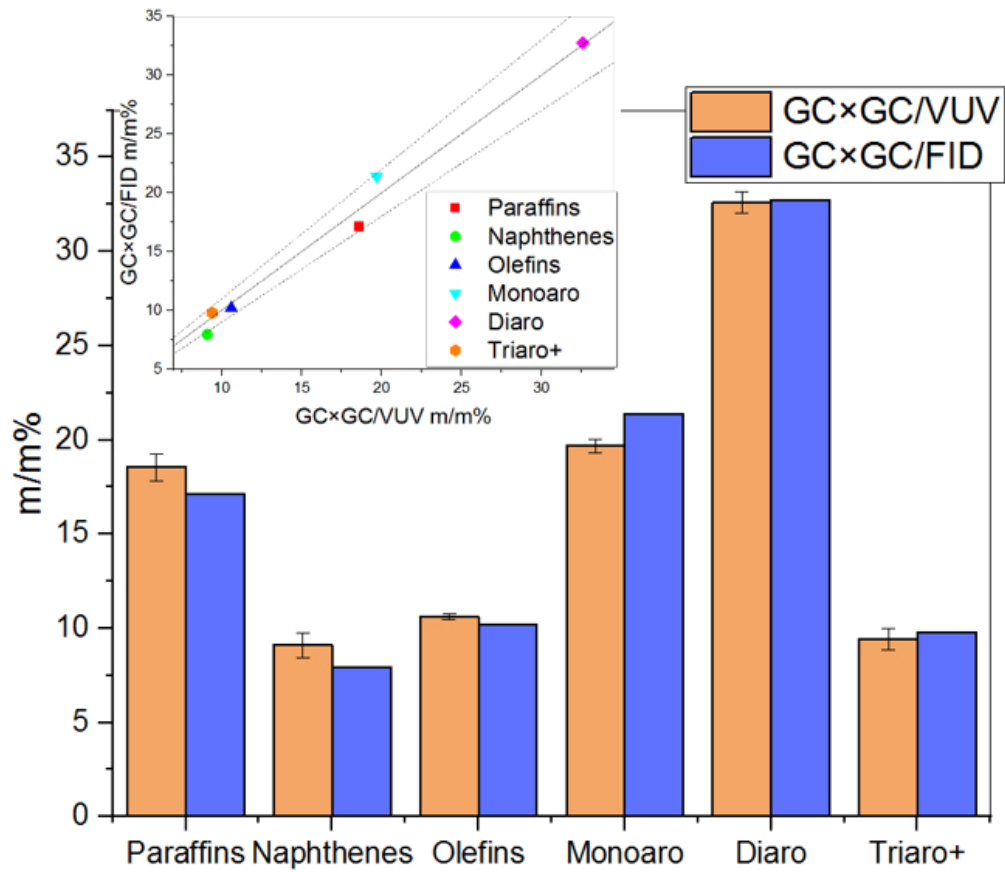


Figure 8 Comparison of the obtained LCO gas oil group type quantification: GCxGC/VUV-average result for three replicates vs. GCxGC/FID with prefractionation. Insert: parity plot; confidence interval $\pm 10\%$.

54x47mm (300 x 300 DPI)

Saturated fraction					Unsaturated fraction										
nC	n-CnH2n+2	i-CnH2n+2	CnH2n	CnH2n-2	CnH2n	CnH2n-2	CnH2n-6	CnH2n-8	CnH2n-10	CnH2n-12	CnH2n-14	CnH2n-16	CnH2n-18	CnH2n-20	CnH2n-22
9	0.95				0.65	0.61	0.39								
10	0.98	0.88	1.23		0.66	0.61	0.41	0.40		0.27					
11	1.02	0.83	1.25	0.99	0.70	0.57	0.44	0.42		0.30					
12	1.02	0.84	1.04	0.90	0.71	0.63	0.47	0.44	0.38	0.31	0.27				
13	1.00	0.89	1.07	0.95	0.72	0.61	0.48	0.46	0.41	0.33	0.30				
14	0.99	0.91	1.01	1.01	0.72	0.65	0.51	0.47	0.43	0.35	0.32	0.34	0.29		
15	0.99	0.94	1.03	1.02	0.73	0.64	0.54	0.48	0.44	0.38	0.34	0.32	0.31		
16	1.00	0.96	1.01	1.00	0.74	0.69	0.55	0.48	0.45	0.42	0.37	0.35	0.32	0.29	
17	1.00	0.99	0.99	0.96	0.74	0.69	0.56	0.51	0.48	0.45	0.40	0.36	0.35	0.28	0.32
18	0.99	0.98	0.98	0.96	0.74	0.66	0.59	0.51	0.47	0.47	0.43	0.41	0.38	0.31	0.34
19	0.99	1.01	0.98	0.94	0.77	0.64	0.60	0.52	0.50	0.51		0.46	0.43		0.38
20	1.00	1.02	0.99	0.94	0.85	0.68	0.62	0.55		0.54					
21	0.99	1.05	0.95	0.95		0.74	0.62	0.58		0.56					
22	0.99	1.02	0.97	0.97			0.64								
23	1.02	1.02	0.93	0.96			0.66								
24	0.99	1.15	0.89												
25	1.00	1.17													

Table 1 VUV RRFs relative to n-C17H36 (125-240 nm Avg. Abs.) for saturated and unsaturated gas oil fraction, average values for 14 gas oils are presented.

136x45mm (300 x 300 DPI)