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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

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2
3 24 to perform direct quantification of hydrocarbons in GOs without prefractionation. VUV RRFs
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5 25 were measured by using a GC×GC-VUV/FID dual detection set-up in which FID was employed
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8 26 as a quantitative reference. In order to obtain VUV RRFs representative for any gas oil, a set of
9
10 27 14 GOs with different origins was employed. Both VUV RRFs averaged in 125-240 nm range
11
12 28 and spectral VUV RRFs (reference spectra) were obtained. It was demonstrated that VUV RRFs
13
14 29 were similar between employed GOs allowing their universal use. Obtained RRFs were used to
15
16 30 perform hydrocarbons quantification for a light cycle oil (LCO) by GC×GC/VUV, with olefins
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18 31 and naphthenes being quantified through spectral decomposition. Good comparability with
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20 32 results obtained by prefractionation was observed demonstrating the great interest of the
21
22 33 GC×GC/VUV approach for the detailed and rapid analysis of hydrocarbons in gas oils.
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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

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3 70 Jennerwein et al. [14] has shown that proper automated identification may be obtained from
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5 71 GC×GC/MS thanks to adequate Visual Basic scripts that take into account specific m/z
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7 72 fragments for a given family. Making this method quantitative required a complex method to
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9 73 determine MS response factors based on the analysis of numerous standards. The obtained
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11 74 response factors may vary from one instrument to another and MS instruments are generally
12
13 75 considered as sensitive instruments that require frequent calibration. That is why most of current
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15 76 GC×GC/MS methods are only semi-quantitative [18] and do not account for response
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17 77 differences between compounds. Finally, MS still fails in discerning compounds that give same
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19 78 fragments and elute in the same region of the 2D chromatographic space such as for example
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21 79 naphthenes and olefins.
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27 80 Newly introduced vacuum ultraviolet (VUV) broad band absorbance detector has recently
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29 81 attracted a lot of attention. Its amenability for oil and gas characterization has already been
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31 82 demonstrated in a number of works [21–26]. VUV detector possesses the ability to differentiate
32
33 83 between different types of compounds based on their spectral signatures, provided that they are
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35 84 sufficiently different [22,27,28]. Additionally, VUV has quantitative abilities according to
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37 85 Beer-Lambert's law, hence it also enables compounds quantification. However, quantification
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39 86 with VUV is not completely straightforward, as different compounds can exhibit various VUV
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41 87 responses. For example, same mass of aromatic species absorbs about 3 times more (depending
42
43 88 on the species) in the 125-240 nm range when compared to saturated ones [21]. Hence,
44
45 89 compound response needs to be corrected by using appurtenant VUV relative response factors
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47 90 (RRFs).
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53 91 VUV RRFs have been reported in several works [21,24,29]. Walsh et al. [21] demonstrated
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55 92 RRFs for the purpose of bulk characterization of gasoline samples (PIONA type analysis).
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57 93 Weber et al. [24] achieved mass percent quantification of saturates, mono, di, and polyaromatics
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3 94 in diesel samples. García-Cicourel and Janssen [29] introduced a GC/VUV method for the
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5 95 measurement of the total level of aromatic hydrocarbons in purified mineral oils.
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8
9 96 VUV has only recently been hyphenated with GC×GC analysis [30–34]. Wang et al. [33] have
10
11 97 demonstrated how an additional dimension of separation provided by VUV in GC×GC/VUV
12
13 98 analysis can allow to resolve coelution of molecules commonly present in diesel samples.
14
15 99 However, the possibility of full quantification of all hydrocarbon families in more complex
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17 100 samples such as gas oils by using VUV RRFs has not yet been reported. This approach would
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19 101 allow to eliminate the need for prefractionation step commonly employed when using
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21 102 GC×GC/FID for GO quantification and render the analysis less time consuming and less costly.
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25 103 The purpose of the present work is to report, for the first time, VUV RRFs for ca. 160 blocks
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27 104 of hydrocarbons in gas oils according to their carbon number. Having such a database of
28
29 105 VUV RRFs has permitted to perform direct quantification of hydrocarbons in GOs by
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31 106 GC×GC/VUV without necessity of prefractionation.
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35 107 Methodology for deriving VUV RRFs involved using a GC×GC-VUV/FID dual detection set-
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37 108 up in which FID was employed as a quantitative reference. In order to obtain VUV RRFs
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39 109 representative for any gas oil, a set of 14 GOs with different origins was employed. To obtain
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41 110 RRFs for hydrocarbon families which coelute in GC×GC analysis (namely olefins/naphthenes),
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43 111 all GOs were prefractionated into saturated and unsaturated fractions by using solid phase
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45 112 extraction on silver modified silica. All fractions and nonfractionated GOs were then analysed
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47 113 by GC×GC-VUV/FID and both VUV RRFs averaged for 125-240 nm range and spectral
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49 114 VUV RRFs (reference spectra per unit mass) were derived. Obtained VUV RRFs were then
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51 115 employed to perform quantification for an LCO type gas oil with a GC×GC/VUV instrumental
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53 116 set-up. Olefins and naphthenes were quantified trough spectral decomposition and quantitative
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3 117 results obtained by GC×GC/VUV were compared with the one obtained by using GC×GC/FID
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5 118 with prefractionation.
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8 119 **2. Materials and methods**

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14 121 Gas oil database employed for this study was composed of 14 samples from different origins,
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16 122 including 1 straight-run gas oil from atmospheric distillation of crude oils (SR), 3 Light Cycle
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18 123 Oils (LCO) from fluid catalytic cracking units, 4 coker gas oils (GOCK), 2 hydroconverted gas
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20 124 oils (HDCGO) and 4 hydrotreated gas oils (HDT). LCOs and coker gas oils are known to
21
22 125 contain large amounts of olefins and diolefins. Gas oils were diluted in n-heptane and toluene
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24 126 before being analysed with GC×GC-VUV/FID or GC×GC/VUV. Gas oil samples were
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26 127 provided by IFP Energies nouvelles.
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31 128 Prefractionation of the gas oils was performed with a preparative LC PuriFlash instrument
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33 129 (Interchim, France), equipped with online UV detector. The following wavelengths were
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35 130 monitored continuously: 200, 254, and 299 nm. Stationary phase consisted of 25 g of silica
36
37 131 Davisil 923 (pre-packed cartridge PF-SILICA GEL DAVISON 923-F0025, Interchim, France)
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39 132 + 7 g of silica impregnated with silver nitrate at 10 m/m% (Sigma-Aldrich), divided into two
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41 133 cartridges of 3ml—prepared by hand and connected in series. Gas oil samples were diluted to 10
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43 134 m/m% in n-heptane. 5 ml of the sample solution were injected (around 0.5 g of sample on
44
45 135 column). Sample elution was performed in the following order: column conditioning with n-
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47 136 heptane (40 ml/min, t = 2 min), elution with n-heptane (40 ml/min, t = 0-1:45 min) and then
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49 137 with CH₂Cl₂/MeOH 9:1 v/v mixture (40 ml/min, t = 1:45-6 min). Collection of fraction
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51 138 containing saturates was t = 0-1:45 min; and for the fraction containing unsaturates t = 1:45-6
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53 139 min. Fractions were evaporated to few ml by gentle evaporation before GC×GC analysis.
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55 140 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 μm; Agilent Technologies, Inc.)
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11 145 was used in first dimension whereas BPX-50 (50% Phenyl Polysilphenylene-siloxane, 3.2 m,
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13 146 0.25 mm ID, 0.25μm; 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 μL 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,
20
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
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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
34
35 157 the measurement of mass flows at FID and VUV exits). VGA-101 (VUV Analytics, Inc.,
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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
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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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3 166 cm/s) in first dimension and 10 ml/min (modulator pressure 6.7 psig, average velocity 296.3
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5 167 cm/s) in the second dimension were applied. In the case of the GC×GC/FID / GC×GC/VUV
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7 168 configuration, lower 2D flow was applied due lower pressure drop as no splitter or restrictor
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9 169 was used. Modulation period was 4.5 s and injection time of the modulator 0.18 s for
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11 170 GC×GC/FID analysis and 0.22 s GC×GC/VUV analysis. Difference in flow modulator
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13 171 injection times for GC×GC/FID and GC×GC/VUV analysis comes from the fact that VUV
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15 172 features additional transfer line and flow cell under constant high temperature, this additional
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17 173 pressure resistance decreases effective flow in the second dimension, hence for GC×GC/VUV
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19 174 higher modulation injection time had to be employed in order to ensure complete flushing of
20
21 175 the modulation channel. VUV conditions were the same as for GC×GC-VUV/FID analysis.
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23 176 FID detection conditions were 325 °C, air flow 350 ml/min, hydrogen 20 ml/min and make-up
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25 177 gas (nitrogen) 25 ml/min, acquisition frequency 100 Hz.

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31 178 Agilent ChemStation B.04.03-SP1 was used for GC method control and FID data acquisition.
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33 179 VUVision™ 3.0.1 software was used for VUV data acquisition. Plug im! software [36] was
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35 180 employed for GC×GC data visualization, baseline and noise correction and spectra extraction
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37 181 from individual template zones. Parameters for data pre-processing used in this work are
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39 182 available in ref [37]. 2DChrom v3.1.0 in-house software was employed for GC×GC
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41 183 chromatogram integration. Template alignment was performed with in-house software
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43 184 “Déformation de masque pour la GC×GC v1.50” partly based on the methodology described in
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45 185 [38].

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52 187 **3. Results and discussion**

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56 189 **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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7 192 easily applicable due to sample complexity, as there is a limited availability of commercial
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9 193 standards for hydrocarbons contained in gas oils. An alternative approach consists of building
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11 194 a sample set of representative gas oils and using them to determine mean VUV reference spectra
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13 195 for lumps of isomers (clusters of structural isomers having the same molecular formula) that
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15 196 are usually separated by GC×GC analysis. A mandatory requirement is that coelutions must be
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17 197 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
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24 199 atmospheric distillation of crude oil) was constructed. To limit coelutions for the determination
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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
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30 202 with GC×GC-VUV/FID with dual detection in split mode. Obtained signal was subjected to
31
32 203 pre-processing, which involved noise reduction, baseline correction and detector blank
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34 204 subtraction. Subsequently, identification templates were applied on all chromatograms
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36 205 (14 saturated, 14 unsaturated fractions and 14 nonfractionated gas oils). Then, calculation of
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38 206 VUV RRFs was performed, where FID was employed as a quantitative reference allowing to
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40 207 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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55 212 profile for the employed model mixture which demonstrates efficient separation of the two
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3 213 groups of interest, namely saturated and unsaturated species. After validation on a test mixture,
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5 214 method was applied to the fractionation of 14 GOs samples contained in the sample set.
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8 215 **3.3. Noise reduction and baseline correction for VUV data**

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11 216 VUV chromatograms for 14 investigated GOs and their fractions were acquired in the 125-240
12
13 217 nm wavelength range. Inherently, VUV chromatograms obtained at high frequencies necessary
14
15 218 for GC×GC analysis are quite noisy. The use of fluidic modulation, which involves high flows
16
17 219 in the 2D column, additionally decreases VUV signal to noise ratio, thus noise reduction is
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19 220 necessary. Baseline correction is also essential as baseline drift is inherent to GC×GC analysis.
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21 221 As VUV generates multichannel data, for reliable VUV spectra reconstruction it is important
22
23 222 that the approach used for both noise reduction and baseline correction is fast, robust and
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25 223 adaptive for each of the wavelengths at which chromatogram is acquired.
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30 224 Baseline correction of the chromatograms was performed by using a dedicated method based
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32 225 on morphological approach which is an improved version of the method originally proposed in
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34 226 [39]. The approach is based on the estimation of a lower envelope of the observed signal which
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36 227 can be regarded as insertion of segments of finite length below the curve and retaining the
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38 228 envelope produced by all the segments. This can be drastically improved in case of strong noise
39
40 229 by calculating the lower envelope from a signal modified by low-pass filter. Considering s the
41
42 230 observed signal, f a low pass filter, and B baseline correction from [39], the corrected signal s^*
43
44 231 is obtained by $s^* = s - B(f(s))$. Noise correction was performed primarily, based on observation
45
46 232 that VUV spectra ought to possess monotonous nature, by choosing an averaging window
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48 233 (number of signal points) for which mean value of the signal will be repeatedly calculated until
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50 234 the entire 125-240 nm range is covered. Additionally to noise and baseline correction, VUV
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52 235 signal demonstrated a detector blank signal which was characterised by higher noise at short
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54 236 wavelengths (close to 125 nm) and long ones (close to 240 nm), which caused artificial
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3 237 deformation of the measured VUV spectra. Average contribution of the detector signal was
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5 238 estimated for a chromatogram section where species do not elute (far end of chromatogram
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7 239 where there is only noise) and this contribution was subtracted at every pixel of the
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9
10 240 chromatogram. Detailed description of all the pre-processing steps along with chosen
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12 241 parameters for data pre-processing used in this work was provided in [37].
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14

15 242 Illustration of the influence of each one of these pre-processing stages on the measured VUV
16
17 243 spectrum is shown in Figure 2. Traced in black is the extracted summed spectrum from the
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19 244 chromatogram zone where olefins and naphthenes coeluted for an LCO type gas oil. This
20
21 245 spectrum was rather noisy and additionally its profile did not correspond to the typical spectrum
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23 246 of an olefin or naphthene from the VUV spectral library (see insert in Figure 2). Further, traced
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25 247 in blue is the spectrum obtained after applying noise correction and outlined in red is generated
26
27 248 spectrum after both noise and baseline correction were applied. Even after noise and baseline
28
29 249 corrections, obtained spectrum demonstrated higher than zero absorbance at wavelengths
30
31 250 longer than 220 nm and even a slight increase of absorbance at 240 nm, which is known not to
32
33 251 be the case for olefins or naphthenes. After additional detector blank signal subtraction, a
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35 252 satisfactory spectrum was obtained (traced in green).
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41 253 **3.4. GC×GC templates application**

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44 254 After appropriate chromatogram pre-processing, identification templates were applied on the
45
46 255 whole sample set consisting of 14 GOs and their fractions. Figure 3 illustrates VUV
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48 256 chromatograms (125-240 nm Avg. Abs.) for unsaturated and saturated GO fractions with
49
50 257 identification templates applied. Templates were designed so as to clearly define zones in which
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52 258 positional isomers with same molecular formula elute. As GC×GC separation was performed
53
54 259 with a classical non-polar / medium-polar column set, the separation of hydrocarbons in the 1st
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56 260 dimension was according to increasing carbon number and in the 2nd dimension according to
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261 their polarity. Thus, on the second dimension compounds were distributed according to
 262 increasing aromatic character. On the first dimension template covered carbon numbers from
 263 C9 to C30. Detailed templates with all molecular formulas corresponding to each template zone
 264 are provided in Supporting Information (Figure S4).
 265 Templates needed to be slightly adjusted each time when applied to another sample, but also
 266 when transferred from FID to VUV data for the same sample despite the use of the splitter. To
 267 facilitate template alignment, automated anchor point estimation by BARCHAN algorithm [38]
 268 was applied and very good template alignment result was obtained for template transformation
 269 from FID to VUV data. For very dissimilar samples however, additional anchor points had to
 270 be applied manually for optimal transformation.

271 3.5. Calculation of VUV RRFs for template zones

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

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

279
 280 with $Area_{FID}^i$ and $Area_{VUV}^i$ representing the measured response areas on the FID and VUV
 281 detectors, respectively for compound i or the reference compound ref , RR_{FID}^i and RR_{VUV}^i
 282 relative response factors for the considered analyte and $K(T)^i$ a temperature dependent

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3 283 correction factor related to flow splitting effects between the two detectors and that can be
4
5 284 determined by the analysis of a mixture of linear paraffins. Details of obtaining Equation 1 and
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7
8 285 calculating temperature dependent correction factor $K(T)^i$ were provided in [40].
9

10
11 286 RRF_{FID} represents in the same way as RRF_{VUV} a multiplication factor, necessary to convert
12
13 287 response area per unit mass of investigated compound into the area per unit mass of the
14
15 288 reference compound. It can be calculated as a ratio of the FID mass response coefficient for
16
17
18 289 compound i and FID response coefficient for a reference compound. Response coefficient for
19
20 290 FID in turn can be calculated according to different approaches, for example relative to benzene
21
22 291 according to ref [41].
23
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25 292 VUV RRFs, obtained in the described way depend only on molecules' cross sections and can
26
27
28 293 be used universally. For calculating VUV RRFs, reference compound or blob whose response
29
30 294 is taken to 1 by convention was chosen to be C_{17} n-paraffin for the GO saturated fraction and
31
32 295 $C_{10}H_{12}$ tetralin peak for the GO unsaturated fraction (Figures 3A and 3B). In order to rescale
33
34 296 VUV RRFs relative to the same reference (*i.e.* n- C_{17}), RRFs calculated in the unsaturated
35
36
37 297 fraction relative to $C_{10}H_{12}$ were corrected by using VUV RRF of $C_{10}H_{12}$ in the nonfractionated
38
39 298 sample where n- C_{17} was taken as a reference.
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42
43 299 Estimation of the RRFs was performed for each template zone with the condition that the
44
45 300 measured FID m/m% is higher than 0.5 %. Mean RRF values from the measurements on the 14
46
47 301 saturated and 14 unsaturated fractions of the database were obtained and standard deviations
48
49 302 were determined. It was observed that RSDs of the estimated RRFs were the lowest when
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51 303 average absorbance at full wavelength range 125-240 nm was considered, hence for the final
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53 304 VUV RRFs estimation this wavelength range was employed. Table 1 provides the list of mean
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55 305 VUV RRFs for ca. 160 lumps of isomers present in gas oils according to their chemical family
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58 306 and their number of carbon atoms. Comprehensive list of all obtained VUV RRFs along with
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3 307 appurtenant RSDs for each template zone is provided in the Supporting Information in Tables
4
5 308 S2 and S3. It was observed that despite wide variety of analysed samples, VUV RRFs for the
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7 309 same GO template zone were rather comparable, with weighted relative standard deviation of
8
9 310 less than 20% and often less than 10%. It can be assumed that this variation was due to small
10
11 311 composition variability between GOs, small imperfection of template alignment and limited
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13 312 sensitivity of the VUV. However, these variations were not of strong significance and as such
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15 313 determined VUV RRFs could have been employed universally for the analysis of gas oils from
16
17 314 different origins and without further calibration. In Tables S2 and S3 also reported are average
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19 315 VUV RRFs calculated for each hydrocarbon family and pooled RSDs. These values are well in
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21 316 line with VUV RRFs already reported for PIONA type compounds [21].
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25
26 317 Figure 4 illustrates calculated VUV RRFs (average for 14 GOs) on the 125-240 spectral range
27
28 318 for several hydrocarbon families according to their carbon number. n-paraffins exhibited VUV
29
30 319 response factors which were rather constant (around 1.0) in the observed range of the number
31
32 320 of carbon atoms, which is in accordance to theory. As aromatic species absorb more VUV light,
33
34 321 their response factors were smaller than the one obtained for saturates. Additionally, RRFs for
35
36 322 aromatic species demonstrated an increasing trend with the increase of the number of carbon
37
38 323 atoms. This was explained by the fact that the response factors calculated in this study were
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40 324 given per unit of mass. When increasing the number of carbon atoms within a given family,
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42 325 alkyl chains are growing while the aromatic core that is the major UV absorbing chromophore
43
44 326 remains the same. Hence, molar absorptivity is almost constant (even if some inductive effects
45
46 327 can slightly modify the VUV absorbing properties of the aromatic core) whereas the mass
47
48 328 absorptivity is decreasing due to the dilution effect of alkyl chains. With the increase of
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50 329 aromatic character and degree of unsaturation for following hydrocarbon families, a decrease
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52 330 of estimated VUV RRFs was also observed, indicating increased VUV absorbance.
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331 **3.6. Extraction of reference VUV spectra**

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3 332 GC×GC analysis of gas oils results in certain coelution events no matter the column set
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5 333 employed. Namely, certain template zones in the GC×GC chromatogram contain a mixture of
6
7 334 saturated and unsaturated species. For example, all zones with general formula C_nH_{2n} or C_nH_{2n-2}
8
9 335 contain mixture of olefins and naphthenes. Blobs with formula C_nH_{2n-6} and C_nH_{2n-8} contain
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11 336 monoaromatics and polynaphthenes which coelute. To discern relative quantities of these
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13 337 species in their mixture, spectral dimension or more specifically reference spectra per unit mass
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15 338 can be employed.

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20 339 Reference spectra per unit mass were determined in the same way as VUV RRFs, by using the
21
22 340 FID response as a quantitative reference, and by making a correction for flow splitting effects.
23
24 341 In this way, obtained reference spectra represented, contrary to epsilon (molar absorptivity) in
25
26 342 the Beer-Lambert law, not molar relative values but mass relative values. They corresponded
27
28 343 to mass attenuation coefficients (which are the molar absorptivity divided by the molecular
29
30 344 weight). Reference spectra were determined for a reduced sample set consisting of 7 GOs (LCO
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33 345 and GOCK), chosen as they are expected to contain significant amounts of olefins.

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36 346 First VUV summed spectra for each template zone were extracted by using Plug im! software
37
38 347 [36]. Then, VUV reference spectra per unit mass were calculated for saturated fraction and
39
40 348 scaled to n-C₁₇ spectra which was chosen as a reference (its max absorbance was set to 1). For
41
42 349 unsaturated fraction C₁₀H₁₂ tetralin peak was employed as a reference. All spectra from
43
44 350 unsaturated fraction were scaled again as tetralin spectrum relative to n-C₁₇ was determined
45
46 351 through the analysis of unfractionated GO. Then average values for all 7 gas oils were
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48 352 determined.

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52
53 353 Figure 5 shows several examples of the obtained spectra, all scaled to n-C₁₇. Figures 5A, 5B
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55 354 and 5C show spectra for n-paraffins, i-paraffins and non-condensed naphthenes according to
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57 355 increasing carbon number. Spectra for saturates were relatively uniform, which was in line with
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3 356 previous findings [21]. Figure 5D shows reference spectra for olefins with a clear reduction of
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5 357 absorbance per unit mass with increasing carbon number. The same is observed for
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7 358 alkylbenzenes in Figure 5E and naphthalenes in Figure 5F. Shape of the spectra fitted well with
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9
10 359 the expected features observed for similar compounds in the VUV spectral library. A
11
12 360 bathochromic shift of the maximum absorbance as well as an absorbance increase was observed
13
14 361 when aromaticity is increasing. On the contrary, naphthenes and paraffins (n- or iso-paraffins)
15
16 362 were hardly distinguishable and their separation with the only spectral dimension was not
17
18 363 possible. Separating these compounds thus requires a prior satisfactory chromatographic
19
20 364 separation. Olefins and naphthenes demonstrated very different VUV spectra, so did
21
22 365 polynaphthenes and monoaromatics, and their spectral differences open the way to
23
24 366 quantification through spectral decomposition. Importantly, differences between the spectra
25
26 367 within the same family of compounds were observed. For example, in the case of the
27
28 368 monoaromatics spectra (Figure 5E), significant difference in absorbance per unit mass between
29
30 369 individual monoaromatics species was observed. Thus, more accurate quantification result can
31
32 370 be obtained if individual VUV RRFs are used when compared to conventional class based
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34 371 approach [21].
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41 372 **3.7. Spectral decomposition: application to naphthenes/olefins quantification**

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43 373 As previously stated, common problem in group type quantification in gas oils is the
44
45 374 quantification of coeluting species, such as olefins and naphthenes. VUV reference spectra
46
47 375 obtained as previously described can however be employed to derive contribution of each of
48
49 376 the two families to their mixture spectra. In the zone where olefins and naphthenes commonly
50
51 377 coelute, observed spectrum for the gas oil is indeed a linear combination of two reference
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53 378 spectra, thus it is possible to calculate the proportion of each of the two families (see Supporting
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55 379 Information Section S4 for more details on calculations).
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3 380 For the determination of the total amount of olefins and naphthenes in the gas oil, a single
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5 381 template zone was constructed by unifying all zones corresponding to molecular formula C_nH_{2n}
6
7 382 or C_nH_{2n-2} . (see insert in Figure 6A). Figure 6A shows obtained reference VUV spectra per unit
8
9 383 mass. Traced in blue is the reference spectra for naphthenes averaged for 14 saturated gas oil
10
11 384 fractions. In red is the reference spectra for olefins averaged for 7 olefin containing gas oils.
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13 385 Shaded zones illustrate obtained standard deviation of the spectra (up to 10%). It can be seen
14
15 386 that the variability is the highest for lower wavelengths, however spectra were still very
16
17 387 comparable between different gas oils. Calculated VUV RRFs for this zone were 0.7 for olefins
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19 388 and 1.0 for naphthenes.

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23
24 389 These spectra can be further employed for estimation of their linear combination in their
25
26 390 mixture spectra obtained for the nonfractionated gas oil for the same template zone. Figure 6B
27
28 391 shows traced in black measured spectrum for olefin/naphthene zone for a nonfractionated gas
29
30 392 oil of LCO type. Calculated contribution of reference olefin (red) and naphthene (blue) spectra
31
32 393 correspond to the multiplication of the reference spectrum by the proportion of each species
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34 394 estimated through spectral decomposition. In green is the calculated spectrum which corresponds
35
36 395 to 53% contribution of olefin and 47% of naphthene. Good fit was obtained between measured
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38 396 and calculated spectrum.

389 **3.8. Application of VUV RRFs and spectral decomposition for the GC×GC/VUV** 390 391 **analysis of gas oils**

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399 Example of application of VUV RRFs and spectral decomposition for estimation of total
400
401 quantity of olefins and naphthenes is given for an LCO type gas oil. Figure 7 shows the
402
403 comparison of the generated hydrocarbon distribution according to carbon number for an LCO
404
405 type gas oil by using GC×GC/FID with prefractionation and by using GC×GC/VUV in
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407 combination with VUV RRFs. For olefins/naphthenes zone, spectral decomposition was
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409 applied first. After having determined the ratio of olefins and naphthenes, a mean VUV RRF

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3 405 for this zone was calculated (based on their RRF values mentioned above) and applied to
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5 406 estimate quantity of olefins and naphthenes.
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8 407 Figure 8 shows obtained group type quantification for the same gas oil where quantity of major
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10 408 hydrocarbon families was reported. Very good agreement between VUV data and FID data was
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12 409 obtained with bias lower than 10% (see insert in Figure 8).
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20 411 **Conclusion**

21
22 412 The purpose of this work was to report, for the first time, VUV RRFs for all hydrocarbon lumps
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24 413 (ca. 160) in GOs, permitting to perform their direct quantification by using GC×GC/VUV. Both
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26 414 VUV RRFs averaged in 125-240 nm range and spectral VUV RRFs (reference spectra per unit
27
28 415 mass) were obtained, thus enabling spectral decomposition for coeluting species. These data
29
30 416 were used to quantify hydrocarbons in an LCO gas oil by GC×GC/VUV according to their
31
32 417 family and their number of carbons. Good agreement was obtained between the results of
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34 418 GC×GC/VUV quantification and the results of GC×GC/FID with prefractionation which
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36 419 demonstrated the feasibility and the interest of the GC×GC/VUV analysis for quantification of
37
38 420 hydrocarbons in GOs.
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27 576 **List of Figures**

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29
30 577 Figure 1 Illustration of the methodology for the determination of VUV RRFs for gas oils
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32 578 quantitative analysis.
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36 579 Figure 2 Extracted summed VUV spectrum for olefins template zone for an LCO type gas oil:
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38 580 spectrum without pre-processing (in black), spectrum with noise reduction (in blue),
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40 581 spectrum with noise and baseline correction (in red) and spectrum with noise, baseline
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42 582 correction and detector blank signal subtraction (in green). Insert: example of the VUV
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44 583 spectrum of an olefin (1-tetradecene) and naphthene (ethylcyclohexane) from
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46 584 VUVision® spectral library.
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50 585 Figure 3 VUV chromatogram (125-240 nm Avg. Abs.) for A) coker GO unsaturated fraction
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52 586 and B) coker GO saturated fraction. From bottom to top, template contains following
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54 587 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-}
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56 588 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}.
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3 589 Figure 4 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for selected hydrocarbon
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5 590 families.

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8 591 Figure 5 Reference VUV spectra per unit mass (125-240 nm) relative to n-C₁₇H₃₆ for: A) n-
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10 592 paraffins; B) i-paraffins; C) non-condensed naphthenes; D) olefins; E) alkylbenzenes;
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12 593 F) naphthalenes.

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16 594 Figure 6 A) Average reference spectra per unit mass generated for olefins/naphthenes
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18 595 template zone for saturated and unsaturated gas oil fractions, shaded zones illustrate
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20 596 obtained standard deviation; insert: gas oil template zone for olefins and naphthenes
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22 597 spectra extraction and B) Illustration of spectral decomposition for an LCO type gas
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24 598 oil, estimated amount of olefin 53 m/m% and naphthene 47 m/m% in the mixture.

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28 599 Figure 7 Comparison of the obtained quantification for the hydrocarbon families depending
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30 600 on their carbon number for an LCO type gas oil: A) GC×GC/VUV LCO
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32 601 direct quantification result and B) quantification result of the GC×GC/FID
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34 602 with pre-fractionation.

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36
37
38 603 Figure 8 Comparison of the obtained LCO gas oil group type quantification: GC×GC/VUV-
39
40 604 average result for three replicates vs. GC×GC/FID with prefractionation. Insert: parity
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42 605 plot; confidence interval ±10%.

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46 606

47 48 49 607 **List of Tables**

50
51
52 608 Table 1 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for saturated and
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54 609 unsaturated gas oil fraction, average values for 14 gas oils are presented.

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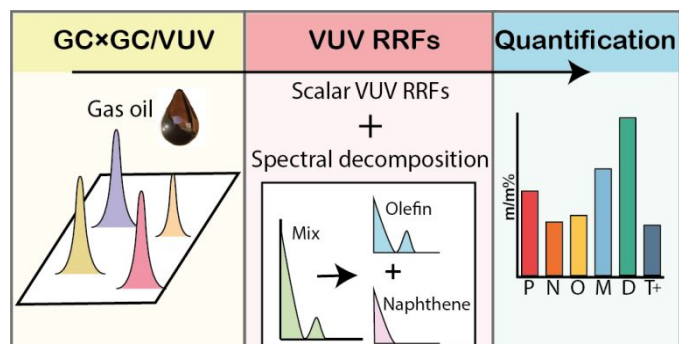
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TOC graphic

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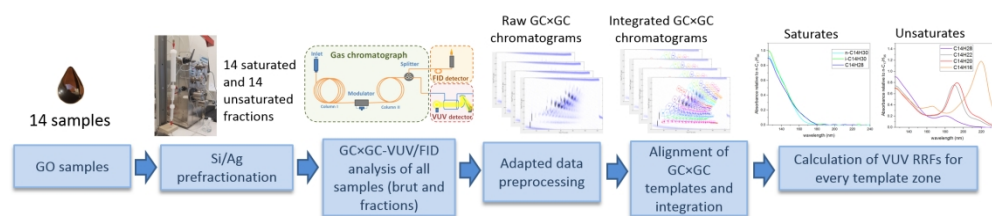


Figure 1 Illustration of the methodology for the determination of VUV RRFs for gas oils quantitative analysis.

197x45mm (300 x 300 DPI)

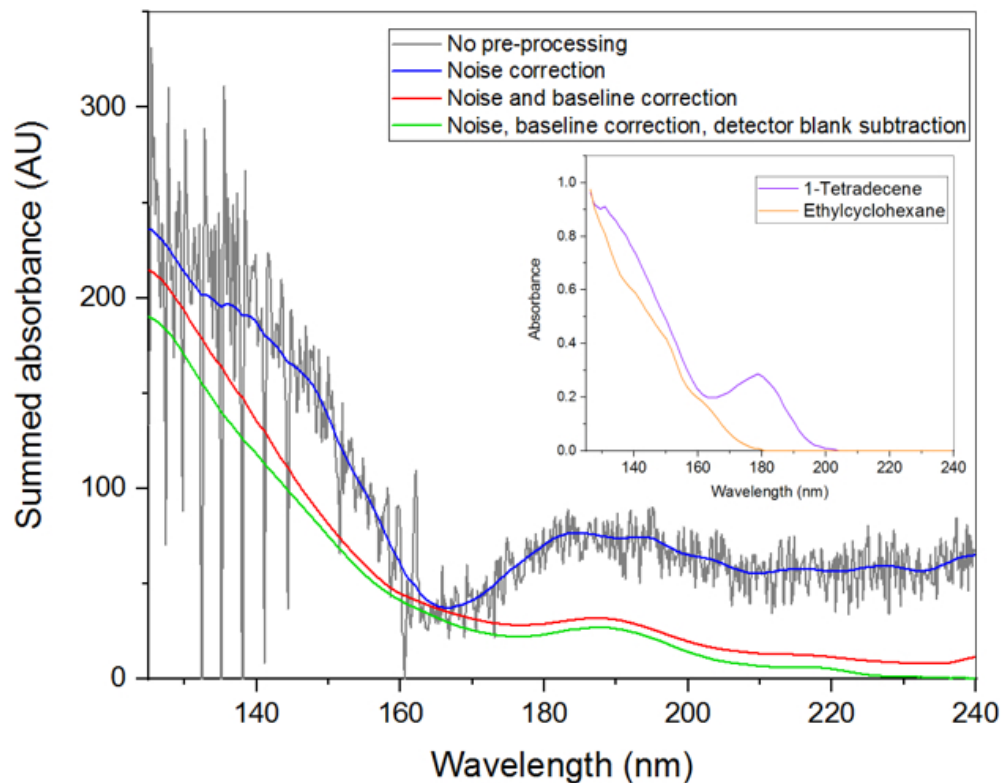


Figure 2 Extracted summed VUV spectrum for olefins template zone for an LCO type gas oil: spectrum without pre-processing (in black), spectrum with noise reduction (in blue), spectrum with noise and baseline correction (in red) and spectrum with noise, baseline correction and detector blank signal subtraction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

53x42mm (300 x 300 DPI)

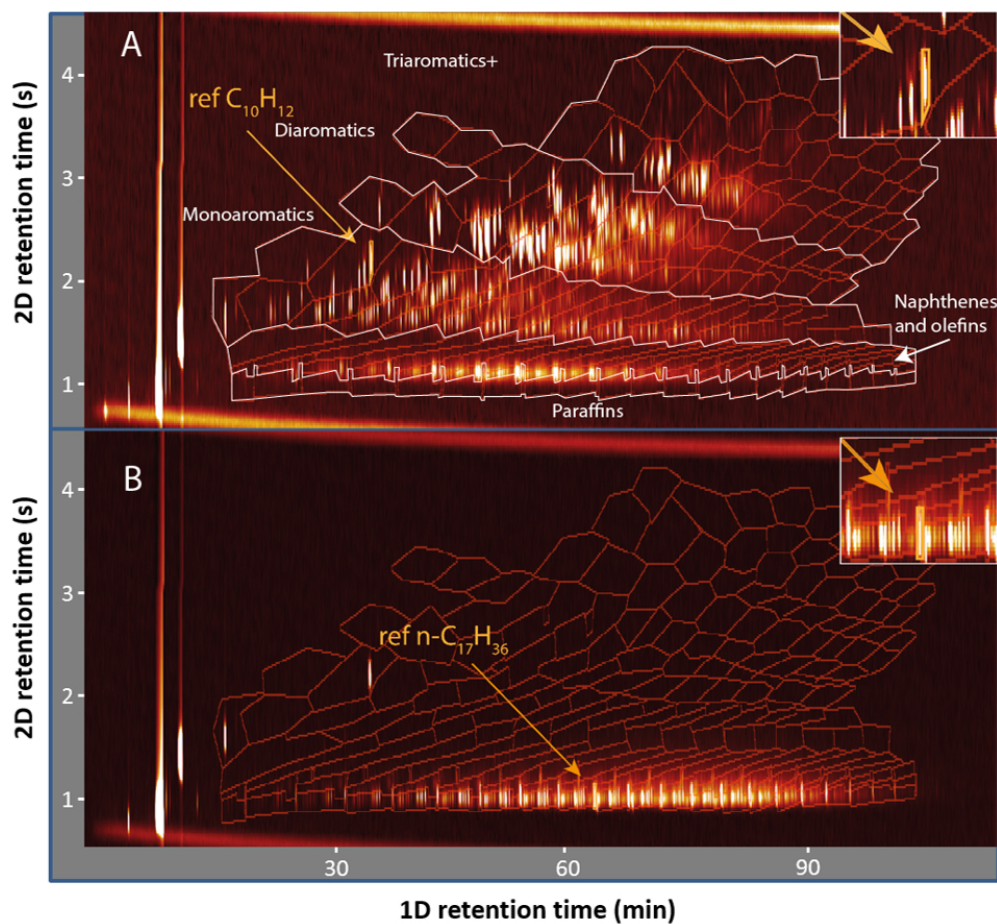


Figure 3 VUV chromatogram (125-240 nm Avg. Abs.) for A) coker GO unsaturated fraction and B) coker GO saturated fraction. From bottom to top, template contains following families of hydrocarbons: n-C_nH_{2n+2}, i-C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}, C_nH_{2n-12},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

81x74mm (300 x 300 DPI)

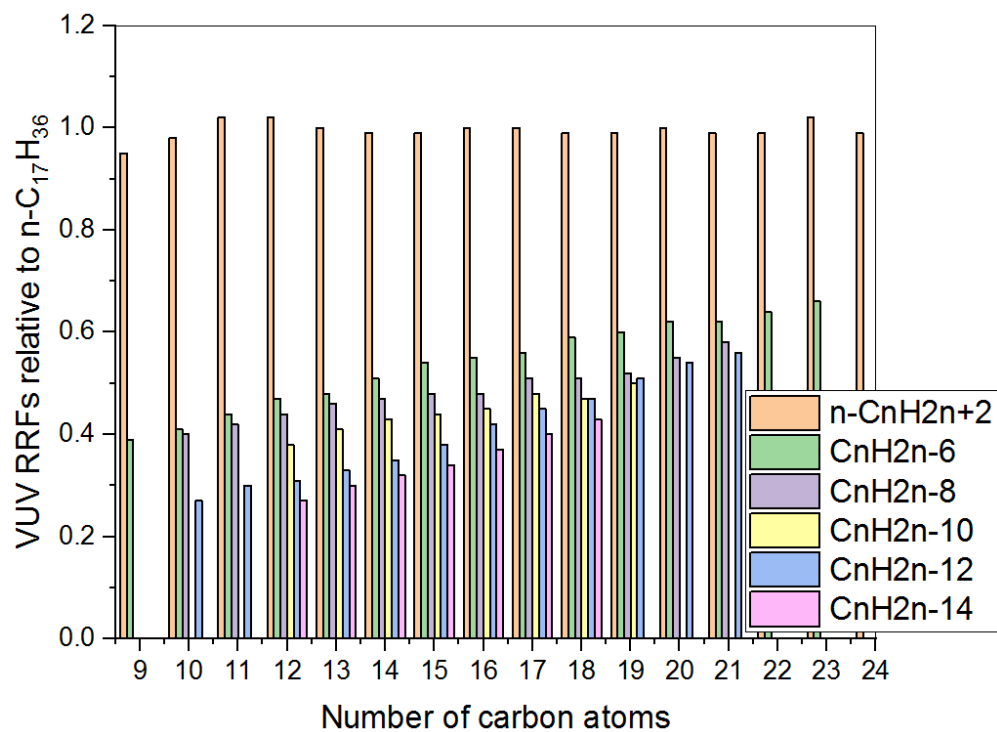


Figure 4 VUV RRFs relative to n-C₁₇H₃₆ (125-240 nm Avg. Abs.) for selected hydrocarbon families.

86x63mm (300 x 300 DPI)

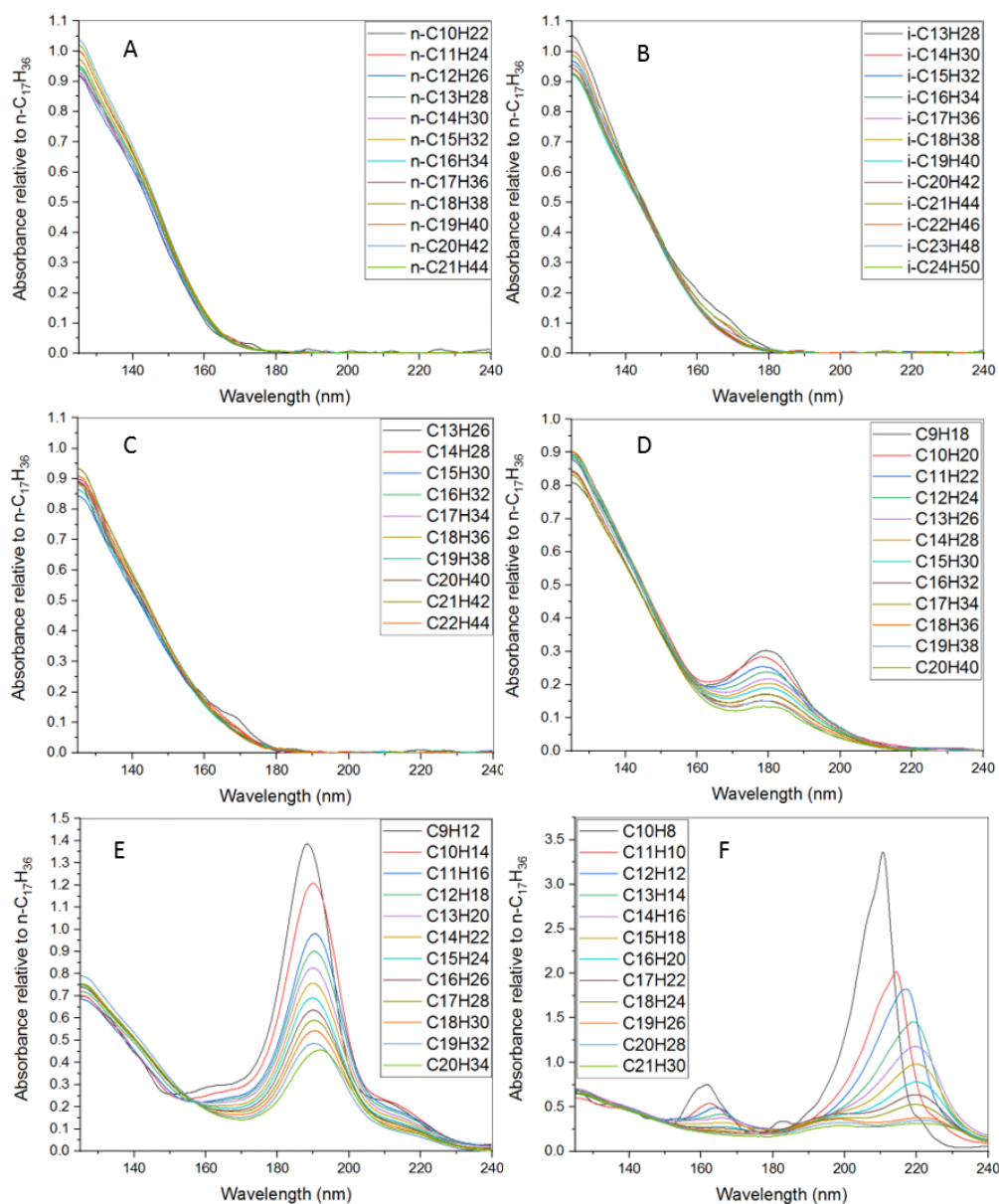


Figure 5 Reference VUV spectra per unit mass (125-240 nm) relative to n-C₁₇H₃₆ for: A) n-paraffins; B) i-paraffins; C) non-condensed naphthenes; D) olefins; E) alkylbenzenes; F) naphthalenes.

74x89mm (300 x 300 DPI)

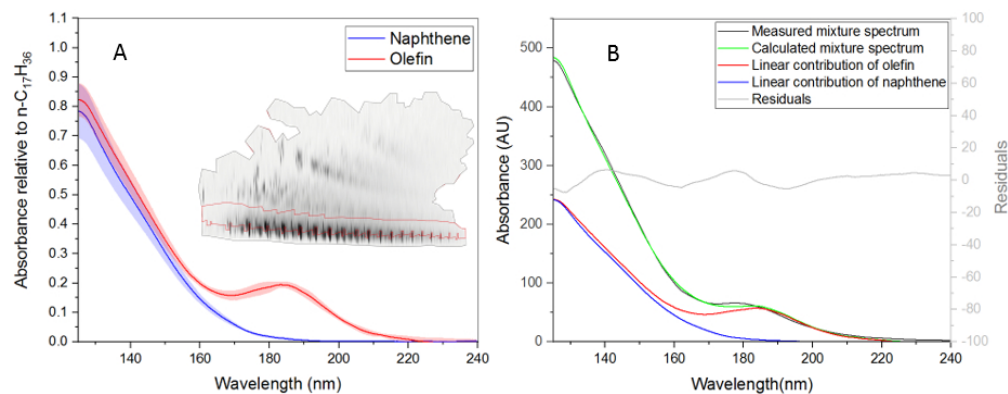


Figure 6 A) Average reference spectra per unit mass generated for olefins/naphthenes template zone for saturated and unsaturated gas oil fractions, shaded zones illustrate obtained standard deviation; insert: gas oil template zone for olefins and naphthenes spectra extraction and B) Illustration of spectral 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)

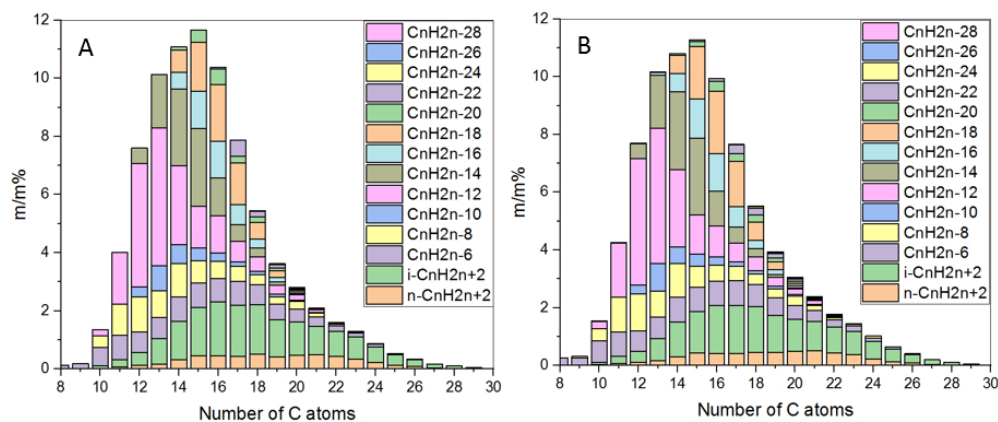
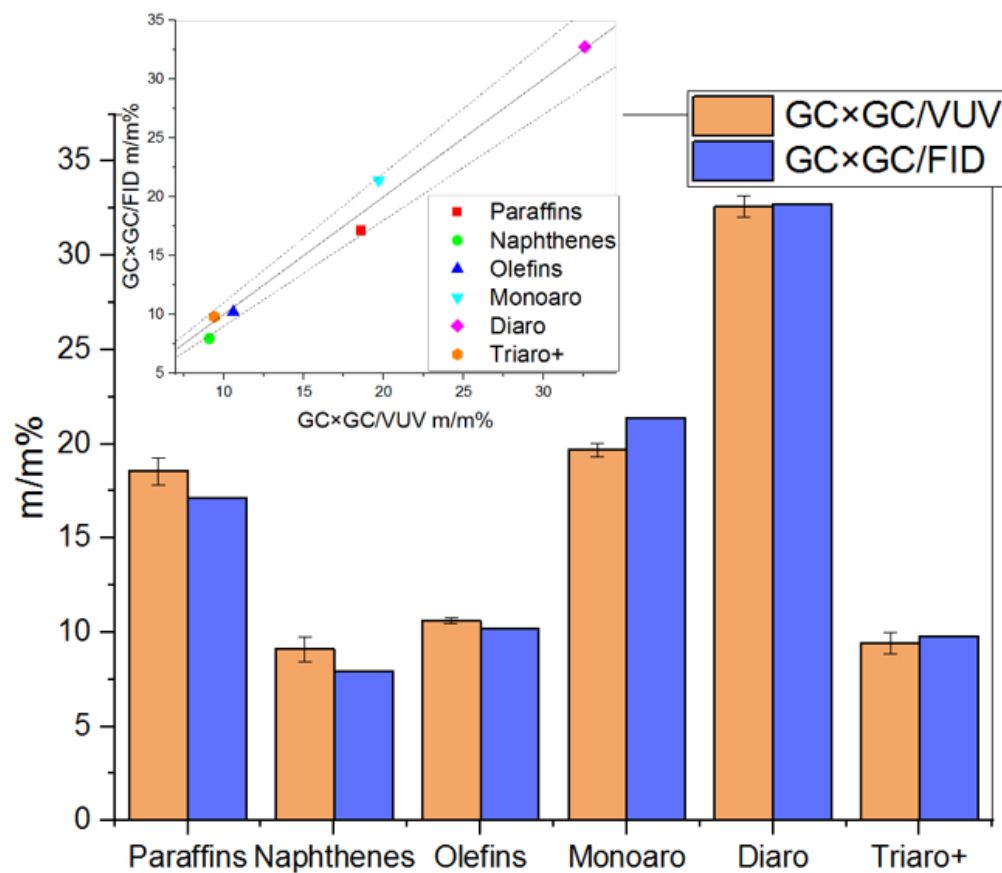


Figure 7 Comparison of the obtained quantification for the hydrocarbon families depending on their carbon number for an LCO type gas oil: A) GCxGC/VUV LCO direct quantification result and B) quantification result of the GCxGC/FID with pre-fractionation.

77x32mm (300 x 300 DPI)



34 Figure 8 Comparison of the obtained LCO gas oil group type quantification: GCxGC/VUV-average result for
35 three replicates vs. GCxGC/FID with prefractionation. Insert: parity plot; confidence interval $\pm 10\%$.
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37 54x47mm (300 x 300 DPI)

nC	Saturated fraction				Unsaturated fraction											
	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)