Quantification of Hydrocarbons in Gas Oils by GCxGC-VUV : Comparison with other Techniques

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Quantification of hydrocarbons in gas oils by GC×GC-VUV - comparison with other techniques

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Abbreviations

^{1}D – First dimension

^{2}D –Second dimension

CFT – Capillary flow technology

CK – Coker

GC×GC – Comprehensive two-dimensional gas chromatography

HDC – Hydrotreated

HDT – Hydroconverted

LCO – Light cycle oil

MMI – Multi mode inlet

SR – Straight-run

VUV – Vacuum ultraviolet absorbance spectroscopy

Key words: comprehensive two-dimensional gas chromatography, vacuum ultraviolet absorbance spectroscopy, middle distillate, quantification

Abstract

Insight into the composition of middle distillates is essential to meet the requirements for product quality, but also in terms of complying to ever more stringent environmental regulations. Newly introduced Vacuum ultraviolet absorbance detector (VUV) possesses both quantitative and qualitative abilities and is amenable to hyphenation with comprehensive two-dimensional gas chromatography (GC×GC). It has good selectivity for hydrocarbon species and permits their differentiation even if they are not chromatographically separated. In this study, quantification of hydrocarbons in 14 gas oils coming from different origins was performed in order to evaluate the benefits of GC×GC-VUV for the analysis of middle distillates. Coelutions between hydrocarbon families were investigated and spectral decomposition carried out for quantification of coeluting hydrocarbon families. Quantification obtained with GC×GC-VUV was compared with conventional techniques such as GC×GC-FID with prefractionation, MS method based on ASTM D2425, UV spectroscopic analysis and bromine number. In general, good comparability was obtained between GC×GC-VUV and all the different techniques for major hydrocarbon families, however with a gain in time and/or information when using GC×GC-VUV. This demonstrates that GC×GC-VUV can be considered as a relevant tool for the detailed analysis of middle distillates, regardless of their origin.

1. Introduction

Middle distillates are complex volatile samples consisting primarily of various hydrocarbons in which number of C atoms normally ranges from C13 to C25 [1]. Owing to their complexity, the use of 1D-GC for the non-targeted characterization of gasoil samples is often limited to simulated distillation and does not permit a group type analysis due to important coelutions. For the quantification of hydrocarbons in middle distillates, rather MS or multidimensional chromatography techniques are employed [1]. For example, ASTM D2425 method relies on mass spectrometry, and enables quantification of 11 families of hydrocarbons [2]. However, this analysis is restricted to samples with a limited boiling point range (160–343 °C) and olefin content below 5 m/m%. Moreover, quantification and calibration are challenging. For detailed hydrocarbon quantification in gas oils, comprehensive two-dimensional gas chromatography in combination with mass spectrometry (GC×GC-MS) [3,4] can also be used but MS still fails in differentiating isomers such as naphthenes and olefins and quantification can be tedious. It is also possible to perform quantification of hydrocarbons by using GC×GC-FID [5,6]. This technique, with the help of identification templates, allows to achieve quantification of all main hydrocarbon families according to groups of isomers with different C number in the middle distillates' distillation boiling point range. However, as FID is a quantitative detector providing no qualitative information, sample prefractionation is necessary for the quantification of hydrocarbon families which are coeluting in order to separate these species prior to chromatographic analysis [7]. Prefractionation however adds additional steps to the analysis, increases analysis cost and may be a source of possible analytical errors due to possible incomplete separation.

Recently introduced vacuum ultraviolet broad band absorbance detector (VUV) [8] possesses both quantitative and qualitative capabilities, and is amenable to coupling with GC×GC analysis. Particular strength of this detector is its universal detection capability, with many compounds exhibiting diverse spectral features. Owing to Beer-Lambert law which is linear and additive, this VUV spectral diversity enables spectral mixtures estimations for coeluting species [9]. Several research works have demonstrated the power of the VUV technique for mixture estimation of coeluted species even if there is no temporal resolution between them [10–14]. This detector has been mostly studied in the field of oil and gas analysis [8,9,15–18] and its unique features have enabled introducing an ASTM standard D8071 for the PIONA analysis of gasoline [19] and more recently ASTM D8267 for jet fuel analysis [20].

First report regarding VUV detector coupling with GC×GC was published in 2016 and since then, application of GC×GC-VUV has been dedicated to gasoline, middle distillates and/or crude oil analysis [21–23], polar VOCs in breath gas [24], bio-diesel fuel and fatty acid samples [25]. These works have demonstrated the preservation of good peak shape and resolution of the GC×GC analysis with various benefits in terms of discrimination of compound classes trough spectral filtering, use of spectral decomposition for coeluting species but also the possibility of pseudo-absolute calibration. Despite 1D-GC-VUV being extensively studied for the detailed hydrocarbon analysis of gasoline, there were no recent studies regarding detailed group type hydrocarbon quantification in gas oils. For gas oils, hyphenation between GC×GC and VUV may aid in overcoming the challenges of the conventional analysis techniques, especially resolving coelutions between different families of hydrocarbons.

Due to this reason, in our previous work [26] GC×GC-VUV was used in order to obtain qualitative and quantitative information regarding the hydrocarbon composition of a gas oil sample. The applied strategy consisted in acquiring a GC×GC-VUV chromatogram of a gas oil and then applying an identification template delineating groups of hydrocarbon isomers according to their family and carbon number. Since all hydrocarbons do not have the same VUV absorbance per unit mass, appropriate relative response factors (RRFs), were determined according to the methodology based on gas oil prefractionation and analysis by GC×GC/VUV-FID [26,27], and were subsequently applied for converting absorbance into m/m% quantitative information. For chromatogram zones in which coelutions between different hydrocarbon families exist, specifically olefins/naphthenes zone, spectral decomposition was applied to deduce their individual quantities. For the investigated real gas oil sample, hydrocarbon quantification obtained by GC×GC-VUV was compared with the result of GC×GC-FID analysis with prefractionation. A good agreement between the two obtained quantification results was observed (within ±10%) however with a gain in analysis time and resolution for coeluters when using GC×GC-VUV.

In the present work, the scope of the previous study is extended, and quantification is performed for a larger sample-base of 14 gas oil samples coming from different origins or processes. Moreover, methodology for accurate group type quantification was improved. Namely, other coelutions than the one between olefins and naphthenes (olefins/iso-paraffins or monoaromatics/polynaphthenes coelutions) were taken into the account. For quantification previously calculated VUV RFFs for gas oils were employed [26]. Obtained GC×GC-VUV quantification results were compared with the results of the other conventional techniques used for hydrocarbons quantification in gas oils such as cryo-GC×GC-FID with prefractionation or

an MS method based on ASTM D2425. Results were also compared with UV spectroscopy which was used for the quantification of mono-, di- and triaromatics in middle distillates but also with bromine number according to ASTM D1159 which is used to characterise the olefine content of a gas oil sample.

2. Materials and methods

The 14 gas oil samples used in this study were provided by IFP Energies Nouvelles, Solaize, France. Gas oils samples were diluted in n-heptane and toluene before being analysed.

For GC×GC-VUV analysis, an Agilent 7890A gas chromatograph equipped with a G3486A CFT forward fill/flush differential flow modulator was employed. Selected non-polar × polar column set consisted of a DB-1 ^{1}D column (100% dimethylpolysiloxane; 20 m, 0.1 mm ID, 0.4 µm; Agilent Technologies, Inc.) and a BPX-50 ^{2}D column (50% phenyl polysilphenylene-siloxane, 3.2 m, 0.25 mm ID, 0.25 µm; SGE Analytical Science). Carrier gas was hydrogen. For all samples, 1 µL injections with a split ratio of 50:1 were performed on a MMI Agilent inlet equipped with a single taper liner with glass wool. Injection port was heated to 300°C, then ramped to 330°C at 500°C/min, where it remained isothermal during 5 min. Initial inlet pressure was 23.2 psig (constant flow: 0.15 mL/min) and initial modulator pressure was 8.33 psig (constant flow: 13 mL/min). Flow in the second dimension is actually slightly lower as column outlet pressure is higher than 0 psig. Oven temperature program was 50 °C (3 min)–325 °C at 2.5 °C min^{-1}. Modulation period was set to 4.5 s, modulation injection times was 0.18 s. Modulation injection time was optimized according to reference [28]. VGA-101 (VUV Analytics, Inc., Austin, TX, United States) detector was employed. VUV conditions were as follows: wavelength range, 125–240 nm; acquisition frequency 33.33 Hz; flow cell and transfer line temperature 325 °C, nitrogen make-up gas pressure 0.15 psig.

Agilent ChemStation B.04.03-SP1 was used for GC instrument control. VUVisionTM 3.0.1 software was used for VUV instrument control and data acquisition. 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” based in part on [29]. Baseline correction and noise reduction and VUV spectra extraction were performed by using plug im! software package for processing of the GC×GC-VUV data [30]. plug im! software was also used for extracting a summed VUV absorbance spectrum from any chromatogram template zone.

GC×GC-FID analysis of neat gas oil samples as well as fractions were performed previously with a column set involving HP-PONA ^{1}D column (100% dimethylpolysiloxane; 20 m, 0.2 mm ID, 0.5 µm; Agilent Technologies, Inc.) and BPX-50 ^{2}D column (50% phenyl polysilphenylene-siloxane, 0.8 m, 0.1 mm ID, 0.1 µm; SGE Analytical Science). Carrier gas was helium, and analysis were run with a constant flow of 1 mL/min. Split injection volume was 0.8 µL with a 1:200 split ratio, injection temperature was 300°C. Oven programming was 60°C to 350°C at 2°C/min. FID detector was operated at 370°C at a 100 Hz frequency. Modulation was performed with a LN2 cryomodulation system from LECO corporation. Modulation period was 8 s with 0.6 s hot jet (hot jet temperature +30°C/oven until 350°C).

The prefractionation step for GC×GC-FID analysis was performed by preparative liquid chromatography [26]. Stationary phase consisted of silver nitrate impregnated silica (Sigma-Aldrich). Saturates species were first eluted with n-heptane, while unsaturates (aromatics and olefins) were collected in a fraction eluted with a mixture of dichloromethane and methanol 9:1.

MS data detailed in this work for comparison with GC×GC-VUV were obtained previously with an in-house method derived from ASTM D2425. According to this method, mass fragments and molecular ions of a hydrocarbon family are summed and used to calculate concentrations from coefficient matrices depending on carbon number. Employed method allows to quantify eleven chemical families in middle distillates, which are given in Table S1 in the Supporting material.

Bromine number of gas oil samples was determined by potentiometry. The analysis was based on ASTM D1159-07 “Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration” [31]. UV analysis for the content of mono, di and tri-aromatic hydrocarbons was performed according to the Burdett method [32].

3. Results and discussion

3.1. Gas oil samples set

The sample set used in this study was composed of 14 gas oils (GOs) from different origins, including 1 straight-run gas oil (SR GO), 3 light cycle oils from fluid catalytic cracking units (LCO GO), 4 coker gas oils (CK GO), 2 hydroconverted gas oils (HDC GO) and 4 hydrotreated

gas oils (HDT GO). Their basic properties are provided in Table 1. Care has been taken to choose samples which reflect a wide variability of compositions and gas oils coming from different processes (Figure 1). Boiling point range was 151-429°C. Sulfur content was comprised between 0.02 and 2.43 m/m% while the saturates content was between 28.9 m/m% and 73 m/m%. As illustrated by the measured values of the bromine number, SR, HDT and HDC gas oils contain low amounts of olefins contrary to LCO and CK gas oils.

Table 1 Properties of selected gas oil samples.

Sample name[a]	Boiling point range[b] (°C)	Saturates[c] (m/m%)	Monoaromatics[c] (m/m%)	Diaromatics[c] (m/m%)	Polyaromatics[c] (m/m%)	Sulfur content (m/m% S)	Bromine number[d] (g/100g)
SR GO 1	221-381	73.0	13.7	11.3	2.0	0.89	2.0
HDC GO 1	199-429	57.4	24.4	12.0	6.2	0.12	4.5
HDC GO 2	180-359	59.6	32.5	6.8	1.1	0.03	1.2
HDT GO 1	184-383	65.0	24.4	8.2	2.4	0.02	0.8
HDT GO 2	187-386	64.8	24.0	8.7	2.5	0.03	0.8
HDT GO 3	211-388	64.3	22.2	9.8	3.7	0.28	1.6
HDT GO 4	210-389	61.5	18.0	13.3	7.2	0.37	1.6
CK GO 1	148-358	60.0	22.7	14.9	2.4	1.48	30.6
CK GO 2	163-371	65.0	20.2	12.8	2.0	1.27	23.2
CK GO 3	188-401	52.8	17.4	22.2	7.6	2.43	26.1
CK GO 4	151-351	62.2	19.1	15.7	3.0	1.40	32.8
LCO GO 1	166-304	28.9	30.8	37.9	2.4	0.22	10.5
LCO GO 2	199-386	34.3	23.3	34.7	7.7	0.95	16.6
LCO GO 3	248-390	40.1	8.6	32.5	18.8	1.11	/

[a]LCO = light cycle oil; CK = coker; SR = straight run; HDC = hydroconverted; HDT = hydrotreated. [b]Reference method ASTM D86. [c]Reference method ASTM D2425. [d] Reference method ASTM D1159.

3.2. GC×GC-VUV measurements

GC×GC-VUV analysis of a gas oil with a non-polar × polar column set results in a structured chromatogram in which compounds elute according to their carbon number in the first dimension and according to polarity in the second dimension. An example of a coker gas oil GC×GC-VUV chromatogram acquired at 125 nm with applied identification template is illustrated in Figure 2A. In the template, individual zones correspond to groups of isomers with different carbon number and belong to fifteen different hydrocarbon families. More detailed template with all molecular formulas corresponding to each template zone is provided in Figure S1 in the Supplementary material.

Identification template has been developed based on the previous GC×GC-MS analysis performed on the SR GO1 sample which was chosen as a reference sample. Additionally, the use of spectral filters in the VUV detection allows to selectively highlight certain hydrocarbon families and verify whether they are properly delineated by the identification template. Figure S2A in the Supplementary material shows the GC×GC-VUV chromatograms of the same coker gas oil at 200 nm. At this wavelength, saturated hydrocarbons and olefins do not absorb, thus it can be seen that the monoaromatics template zone is properly defined. Groups of isomers with different C numbers within each individual family are well separated according to the 'roof tile' effect [33]. Figure S2B shows the same chromatogram at 240 nm. At this wavelength, monoaromatics exhibit hardly any absorbance and diaromatics are easily identified. As all samples were analysed by using the same GC×GC-VUV method, the same identification template was applied for all 14 gas oils. Templates were verified for the need of alignment by using an in-house software "Déformation de masque pour la GC×GC v1.50", however no significant retention time shifts were identified.

In the defined identification template, most of the zones encompass isomers of a single hydrocarbon family. However, certain hydrocarbon families cannot be chromatographically separated, even by using GC×GC analysis. These families have similar volatility and polarity and coelute in the same chromatographic regions. For example, the template zones corresponding to general formula C_nH_{2n} contain mono-olefins which coelute with mono-naphthenes and zones with general formula C_nH_{2n-2} contain di-olefins coeluted with di-naphthenes. These two coeluted groups are present in the coker gas oil chromatogram region designated as 'Naphthenes and olefins' in Figure 2A. Figure 2B shows the same chromatogram at 180 nm wavelength for which saturated compounds (n-paraffins, iso-paraffins and naphthenes) have negligible absorbance thus their peaks cannot be perceived. This chromatogram demonstrates however that olefin peaks extend into the iso-paraffin zone (see insert in Figure 2B) and are not limited only to the C_nH_{2n} elution zones. This is due to the forward fill/flush flow modulated GC×GC analysis which generates wider peaks when compared to cryo modulated GC×GC [34]. It was determined in our study that the olefin quantity coeluting with iso-paraffin family can range up to 20% of the total olefin content. Thus, despite it representing a minor fraction of the total olefin quantity, it has to be taken into account for accurate quantification. Another common coelution occurs in the C_nH_{2n-6} zone where both alkyl-monoaromatics and polynaphthenes can be present. This is also the case in C_nH_{2n-8} zone, however this zone was not considered in our study due to very low abundance of polynaphthenes in the investigated samples.

3.3. GC×GC-VUV quantification methodology

The methodology to obtain hydrocarbon quantification in gas oils consisted in using VUV RRFs calculated for gas oils and reported in our previous work [26] in order to convert VUV absorbance into m/m% information for all template zones where no coelution occurs. For zones where coelutions occur, spectral decomposition has been employed based on reference VUV absorbance spectra. In this study, coelutions were considered in three template zones corresponding to the following general formulas: C_nH_{2n}/C_nH_{2n-2}, i-C_nH_{2n+2} and C_nH_{2n-6}.

The spectral mixture estimation and the resolution of coelutions was performed on the entire elution zones corresponding to each of the three families of compounds, and a summed VUV absorbance spectrum was extracted for the entire family elution zone. The reasons for such an approach, instead of performing spectral decomposition for each individual template zone, were: 1) lack of commercial softwares that can perform the task of automatically estimating spectral mixtures in multiple 2D chromatogram template zones; and 2) possibly better estimation due to higher spectral intensity obtained through summing of absorbances for an entire family. For spectral decomposition by using VUV, sufficient spectral intensity is indeed necessary if one compound is present in low abundance in the mixture compared to the other one [13,14,16].

3.3.1. *VUV reference spectra*

To perform spectral decomposition for the three chromatographic zones of interest, reference spectra per same unit mass (spectral VUV RRFs) for all coeluting families are necessary. As described in our previous study [26], prefractionation on a silver modified silica into a saturated and a non-saturated fraction of a gas oils permits accessing VUV spectral RRFs for all zones where saturated and unsaturated hydrocarbons are initially present together. Figure 3 shows VUV reference spectra that were obtained for saturated and unsaturated families in the three coelution zones of interest, namely: C_nH_{2n} /C_nH_{2n-2}, i-C_nH_{2n+2} and C_nH_{2n-6} from the full set of 14 gas oils (averaged spectra is presented). Olefins and monoaromatics show characteristic absorption bands around ca. 180 - 190 nm that differentiate them from the VUV spectra of saturates (n-paraffins, i-paraffins and naphthenes). Moreover, as these reference spectra exhibit low variability despite a wide gas oils sample set [26], it implies that they can be used to potentially resolve coelutions in a gas oil of any origin.

3.3.2. *Spectral decomposition*

Spectral decomposition aims at calculating the relative amounts of the constituents in a mixture from the measurement of the absorbance spectrum of the mixture. Considering (x) is the measured VUV summed absorbance spectrum for a mixture, a linear combination of the two reference spectra (a and b) is determined so that the distance from x to the vector space spanned by a and b is minimised. See details of the calculation in the Supplementary material in Section 3. Figure 4 illustrates an example of the spectral decomposition performed for all three coelution zones for CK GO 4. Traced in black is the measured mixture VUV spectrum, while in blue and in red are traced calculated contributions of each of the two reference spectra in the mixture. In green is the calculated mixture spectrum. Good fit between measured and calculated spectrum was obtained for all thee coelution zones with minimal residuals (in grey).

3.3.3. *Quantification*

For coelution zones of interest, after performing linear decomposition, an average VUV RRF for each coelution zone for each sample was calculated according to Equation 1.

$$RRF_{mix} = \frac{m}{m}\%_{A} \cdot RRF_A + \frac{m}{m}\%_{B} \cdot RRF_B \qquad \text{Equation 1}$$

Where RRF_{mix} is the average VUV relative response factor for the mixture, $\frac{m}{m}\%_A$ and $\frac{m}{m}\%_B$ are the relative amounts of the two coeluting families in the mixture determined by the spectral decomposition calculation, and RRF_A and RRF_B are the VUV RRFs for the two coeluting families.

Then, m/m% of each template zone was calculated thanks to VUV RRFs and VUV RRF_{mix}. Relative amounts of each family in coelution zones were used to calculate the individual mass percentage of each family and hydrocarbon quantification results were compiled in six chemical groups as indicated in Table 2.

Table 2 Hydrocarbon families quantified by GC×GC-VUV.

Hydrocarbon type	General formula
Paraffins	C_nH_{2n+2}, i-C_nH_{2n+2}
Naphthenes	C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-6}
Olefins	C_nH_{2n}, C_nH_{2n-2}
Monoaromatics	C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}
Diaromatics	C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}
Polyaromatics	C_nH_{2n-18}, C_nH_{2n-20}, C_nH_{2n-22}, C_nH_{2n-24}, C_nH_{2n-26}

3.4. Gas oils GC×GC-VUV quantification results

Figure 5 illustrates the quantification results for major hydrocarbon families obtained with GC×GC-VUV for the 14 investigated gas oils. Detailed results are provided in Table S2 in the Supporting material. Repeatability of the GC×GC-VUV analysis, based on the analysis of three replicates for every sample, was estimated to be up to 5% RSD. An example for repeatability results is given in Table S7. The highest RSDs were obtained for the family of polyaromatics as the quantity of this family was low (<5 m/m% for most investigated gas oils). For all the other hydrocarbon families lower RSD values were obtained, 1.05% RSD in average.

Hydrocarbon quantification obtained by GC×GC-VUV resulted in the relative repartition of individual families which was in line with the origin of the investigated gas oil sample. Only for LCO and CK gas oils measurable quantities of olefins were obtained which was expected as these types of gas oils were not subject to hydrotreatment. SR gas oil exhibited the highest content of saturated species, while LCO gas oils were rich in aromatic species, they demonstrated the highest content of diaromatics while the quantity of monoaromatics was highly dependent on the gas oil initial origin.

3.5. Comparison with other analytical techniques

3.5.1. *Comparison with GC×GC-FID with prefractionation*

Quantification by GC×GC-VUV was compared with GC×GC-FID with prefractionation results for 6 of the 14 gas oils for which GC×GC-FID results were available. Results of the GC×GC-FID analysis are provided in Table S3 in the Supporting material. To obtain hydrocarbon quantification in a gas oil by using GC×GC-FID with prefractionation, the saturated, the unsaturated fraction and the non-fractionated gas oil were analysed by GC×GC-FID and quantitative information was obtained by combining results obtained from these analysis. Figure 6 shows the results of the comparison of GC×GC-VUV and by GC×GC-FID results for major hydrocarbon families. In the figures illustrating correlations, black line represents a parity line, while the dashed lines span the range of ±10%.

For most of the families, good comparability is obtained between the two techniques with the exception of low abundant polyaromatics. This can be in part due to the VUV detector limited sensitivity [35] as for the majority of samples these species were present in low abundance (Table 1). Another reason, and according to us more important, for the observed differences is related to the differences in definition of templates between GC×GC-FID and GC×GC-VUV.

Indeed, GC×GC-FID analysis of this study were performed with cryogenic modulation, a higher modulation period (8 s) as well as different analysis conditions compared to the GC×GC-VUV method. Thus, the chromatographic space occupancy of compounds was slightly different in the two cases, causing the use of different identification template (however with same family repartition) for the GC×GC-FID analysis. Additionally, as templates for GC×GC are made by hand, they are subject to possible differences in families delineation which in turn can cause quantification differences. As a possible consequence, monoaromatics family in Figure 6 seems to be quantified in slightly greater abundance by GC×GC-VUV in some cases and opposite was the case for same gas oils diaromatics and polyaromatics (e.g., HDC GO 1). These differences finally level off, as total aromatics fit well together for the two techniques. It is therefore expected that even better comparability would be obtained between GC×GC-VUV and GC×GC-FID if the same separation conditions were applied enabling to apply the same identification templates. For GC×GC-VUV the use of cryo modulation or reverse fill/flush modulation that generates finer peaks would also be beneficial to improve resolution. For olefins, their quantification seems to be well in line with the one obtained with GC×GC-FID.
Overall GC×GC-VUV provides very similar result to GC×GC-FID however a gain a time is obtained with GC×GC-VUV as it dos not require prefractionation. Additionally, GC×GC-VUV approach can be further refined by extending the spectral decomposition approach possibly to other families, such as sulfur species which coelute with diaromatic and triaromatics hydrocarbons and cannot be distinguished by GC×GC-FID.

3.5.2. *Comparison with MS (method derived from ASTM D2425)*

Figure 7 illustrates the result of the comparison between the GC×GC-VUV and MS hydrocarbon quantification for the 14 gas oils. Results of the MS analysis are provided in Table S4 in the Supporting material.
For paraffins and monoaromatics, good comparability was obtained for most gas oils. Diaromatics and polyaromatics demonstrated some discrepancies, the latter due to their low abundance in the majority of the investigated gas oils as previously mentioned. For all gas oils, good results were obtained for the comparison of more global hydrocarbon families: total saturates and total aromatics. However, also in this case as different approaches were used to define the hydrocarbon families' association, certain differences can be perceived for the individual families quantification.
In the terms of advantages of GC×GC-VUV along with the ones mentioned in the previous section, it provides quantification of olefins and naphthenes, while MS provides no information

regarding naphthenes and olefins individual families as they are characterised by the same molecular formula and are thus indistinguishable. Additionally, GC×GC-VUV can provide an access to families' distribution according to carbon number contrary to MS.

We have also performed a comparison of the quantification according to the "conventional techniques" GC×GC-FID and MS, and the result is provided in Figure S3 in the Supporting material. Also for these two methods, a good comparability was obtained for major hydrocarbon families, while some differences can be perceived for individual families, for example mono, di and polyaromatics. This testifies of the sensitivity of the gas oils' hydrocarbon quantification to the approach used and that even conventional methods can provide slight differences in the obtained results. This finding accentuates the fact that more reliable and robust methods for such complex samples' quantification are necessary. For this GC×GC-VUV can be a good candidate as it offers a robust quantification with distribution according to C number and family, good resolutive power for coeluters and permits to avoid the prefractionation step. Possible areas of improvement are related to the lack of databases of VUV RRFs and limited sensitivity of the detector.

3.5.3. *Comparison with bromine number (ASTM D1159)*

Results of the GC×GC-VUV analysis in terms of olefin content were also compared with bromine number values for gas oils obtained according to ASTM D1159 (Table S5 in the Supporting material). Figure 8A demonstrates that a linear trend is obtained, showing that olefin content obtained by GC×GC-VUV is relevant and in good agreement with the reference method in the oil and gas field for aliphatic unsaturates quantification.

3.5.4. *Comparison with UV spectroscopy*

GC×GC-VUV quantification was also compared with the results of UV analysis (Table S6 in the Supporting material) which is often used for the determination of the aromatic content of petroleum samples. Figure 8B shows the comparison of the quantity of the total aromatic obtained with the two techniques for the 14 gas oils, demonstrating good agreement.

4. Conclusion

In this work group type quantification of 14 gas oils coming from different origins was performed by using GC×GC-VUV. VUV detector's spectral mixtures estimation capability was

employed to resolve coelutions between different families of hydrocarbons in three different chromatographic zones: olefins/naphthenes, olefins/iso-paraffins and monoaromatics/ polynaphthenes. GC×GC-VUV quantification results were compared with other conventional techniques used for hydrocarbons quantification in gas oils (GC×GC-FID with prefractionation, MS method derived from ASTM D2425, UV spectroscopy Burdett method for aromatics and bromine index for olefins). A good agreement for major hydrocarbon families was obtained for all techniques, demonstrating the relevancy of GC×GC-VUV for complete hydrocarbon quantification in gas oils. Compared to GC×GC-FID, a gain a time is obtained as GC×GC-VUV does not require prefractionation. While compared to MS analysis olefins' and naphthenes' contents are available, which are inaccessible by the MS analysis method.

Automation of data processing is still required to make GC×GC-VUV a lab routine analysis technique. As a further step, the quantification methodology and spectral decomposition could be further extended to other species, such as for example sulfur species (benzothiophenes, dibenzothiophenes) as they exhibit different VUV spectral signatures compared to diaromatic and polyaromatic hydrocarbons which whom they are coeluting in the chromatographic analysis.

Supporting Information. Supplementary details about MS analysis; Supplementary details about GC×GC-VUV identification template; Calculation of the linear combination of the two spectra; Quantitative results from all employed analysis methods.

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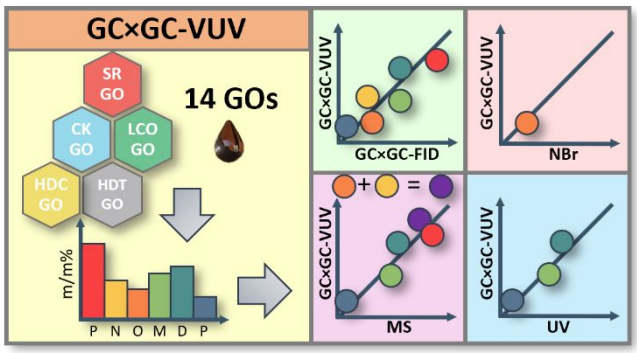
List of Figures

Figure 8 A) Comparison of quantification of olefins in gas oils by GC×GC-VUV and Bromine number for gas oils demonstrates the existence of linear relationship. B) Comparison of gas oil aromatics quantification by GC×GC-VUV and by UV shows good agreement.

TOC graphics



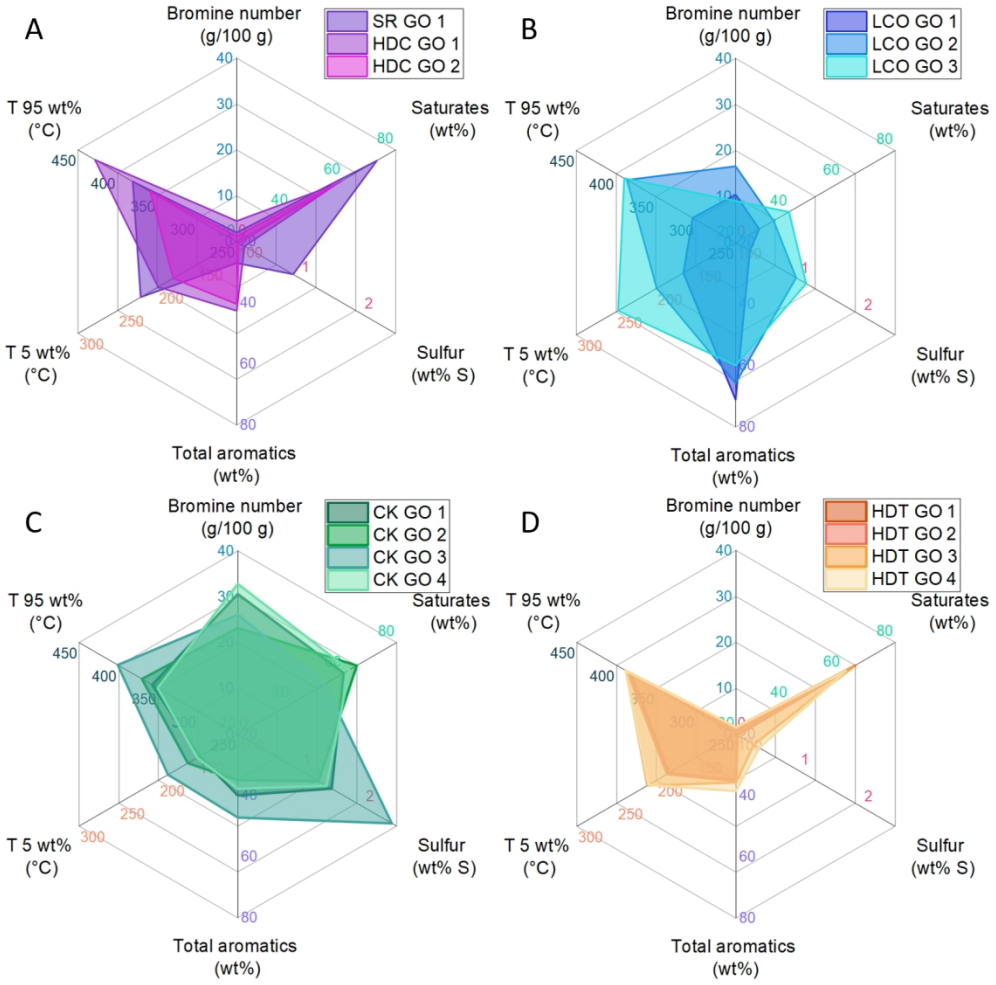


Figure 1 Overview of the physicochemical properties of the selected gas oil samples: A) SR and HDC gas oils; B) LCO gas oils; C) CK gas oils; D) HDT gas oils.

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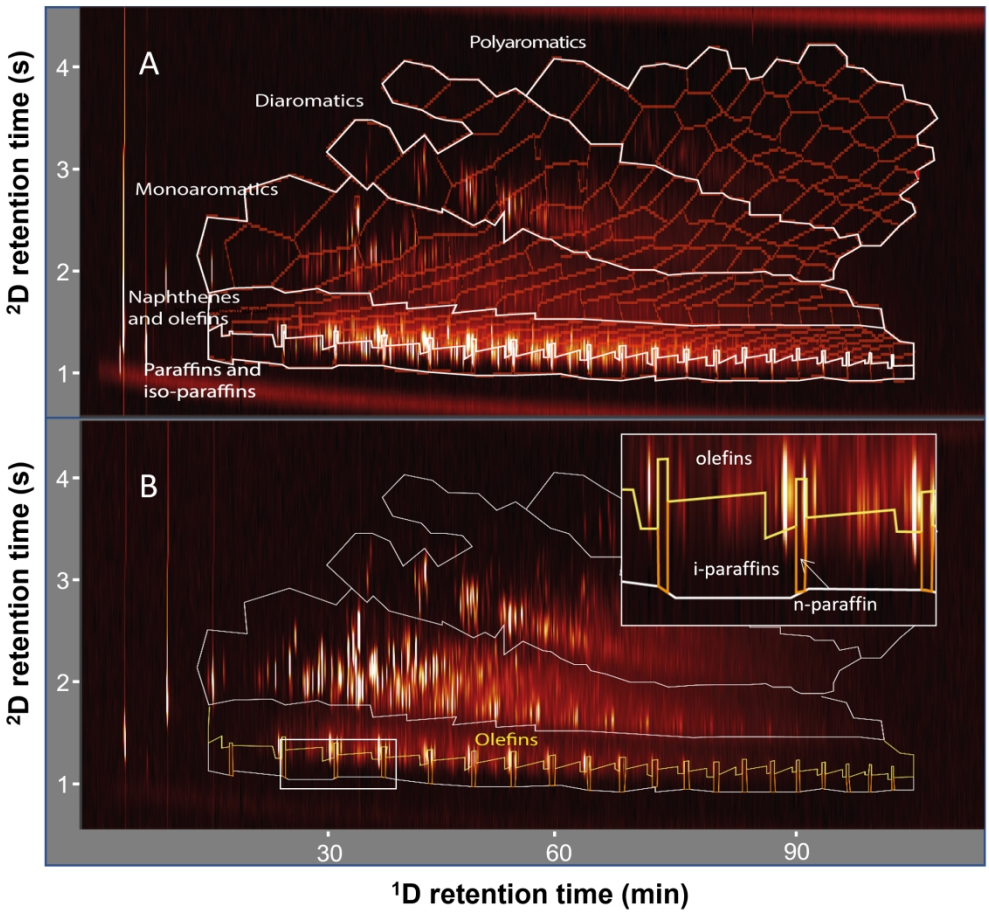

Figure 2 A) CK GO 3 GC×GC-VUV chromatogram (125 nm Abs.) with identification template delineated in orange. Template consists of following families of hydrocarbons (bottom to top): n-CnH2n+2 and i-CnH2n+2, CnH2n, CnH2n-2, CnH2n-6, CnH2n-8, CnH2n-10, CnH2n-12, CnH2n-14, CnH2n-16, CnH2n-18, CnH2n-20, CnH2n-22, CnH2n-24, CnH2n-26.; B) CK GO 3 GC×GC-VUV chromatogram at 180 nm Abs highlights the unsaturated species only; insert: olefin peaks extend into the elution zone of i-paraffins.

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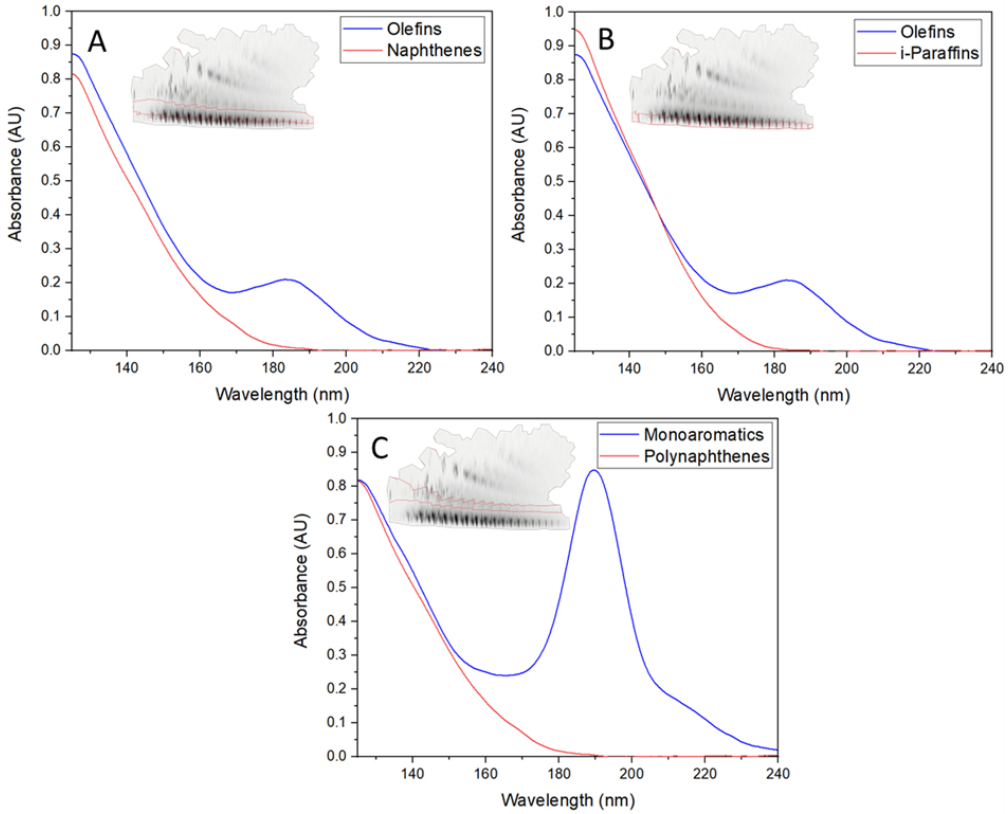

Figure 3 VUV spectral RRFs used for resolving coelutions in gas oils between following families: A) CnH2n/CnH2n-2; B) i-CnH2n+2; C) CnH2n-6; inserts: corresponding zone of chromatogram where the two families coelute.

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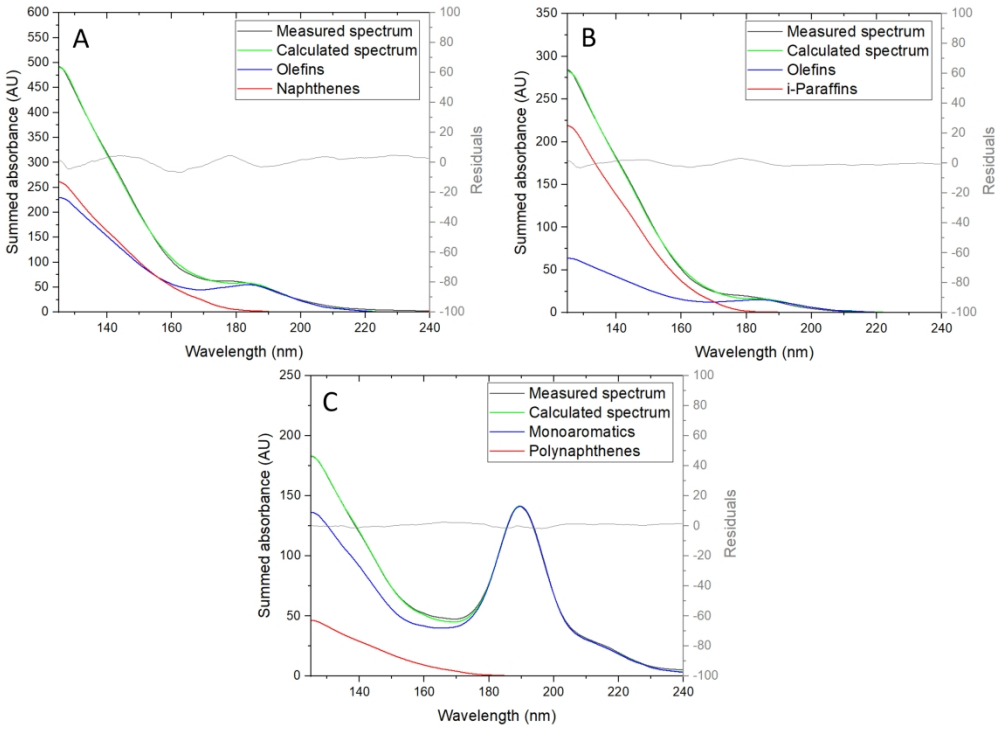

Figure 4 Example of spectral mixture estimation result for three chromatogram zones in CK GO 4: A) CnH2n /CnH2n-2 resulting in 45% olefins and 55% naphthenes, B) i-CnH2n+2 resulting in 24% olefins and 76% iso-paraffins, C) CnH2n-6 resulting in 74% monoaromatics and 26% polynaphthenes. Residuals were estimated as a difference of the measured and calculated spectra.

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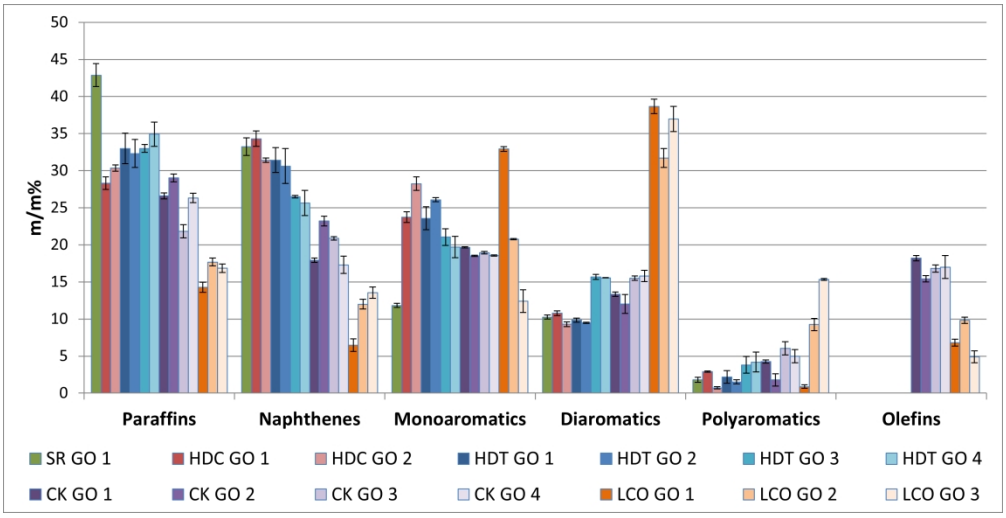

Figure 5 GC×GC-VUV quantification result (average from three replicates) for major hydrocarbon families for 14 investigated gas oils. Obtained compositions are well in line with the gas oil origin; SR gas oil has highest content of paraffins, HDC, HDT and SR gas oils do not show olefin presence, LCO gas oils are rich in aromatic species, CK and LCO gas oils contain olefins.

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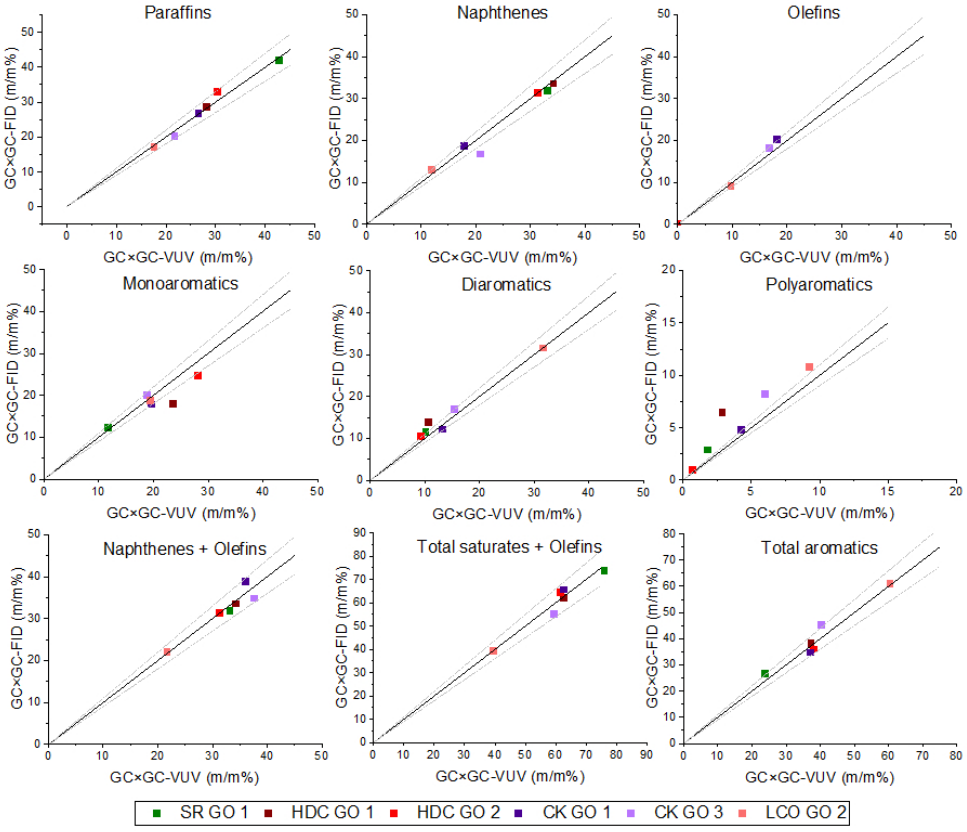

Figure 6 Comparison of the quantification with GC×GC-VUV and GC×GC-FID with prefractionation for major hydrocarbon families for 6 gas oils demonstrates good agreement for majority of families.

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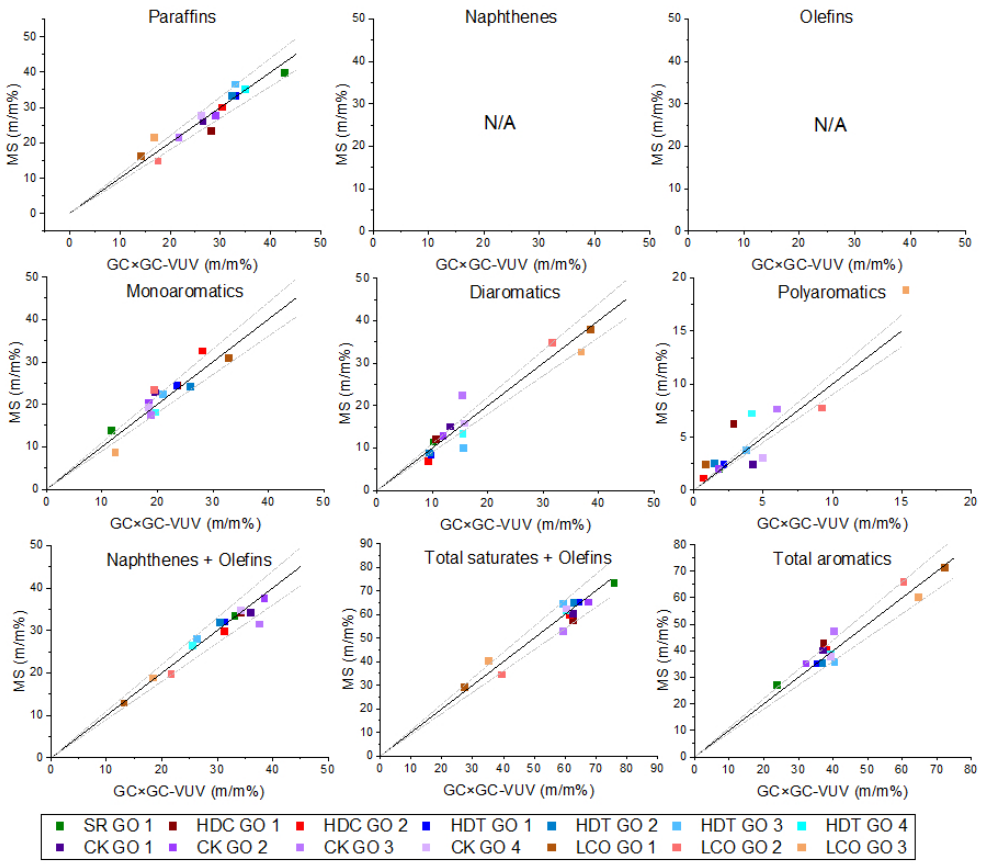

Figure 7 Comparison of the quantification with GC×GC-VUV and MS for major hydrocarbon families for all 14 gas oils demonstrates good agreement for majority of families.

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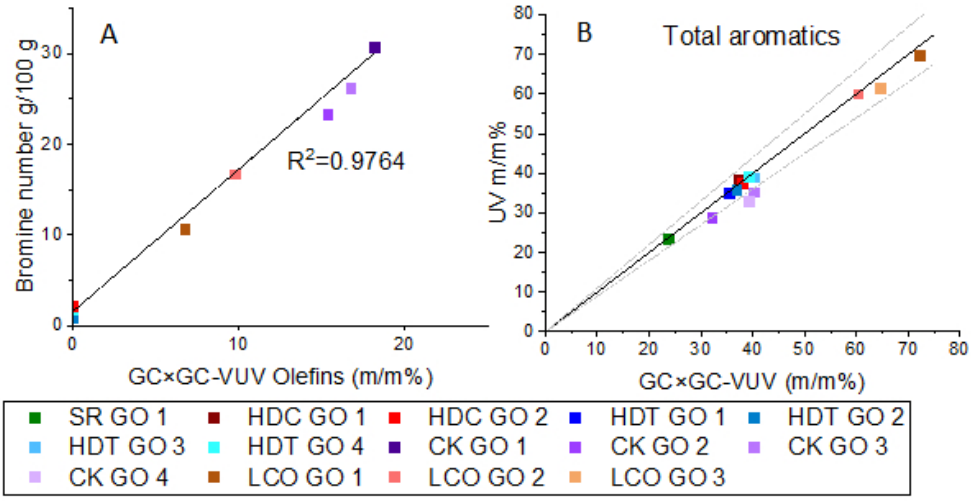

Figure 8 A) Comparison of quantification of olefins in gas oils by GC×GC-VUV and Bromine number for gas oils demonstrates the existence of linear relationship. B) Comparison of gas oil aromatics quantification by GC×GC-VUV and by UV shows good agreement.

51x26mm (300 x 300 DPI)