Novel Four-Dimensional Approach for the Structural Characterization of Neutral Nitrogen compounds in Vacuum Gas oils using UHPLC-IM-QqToF Analysis

Julie Guillemant, Alexandra Berlioz-Barbier, Luis P. de Oliveira, Marion Lacoue-Nègre, Jean-François Joly, Ludovic Duponchel

Novel four dimensional approach for the structural characterization of neutral nitrogen compounds in vacuum gas oils using UHPLC-IM-QqToF analysis

Julie Guillemant†, Alexandra Berlioz-Barbier*†, Jérémie Ponthus†, Luis P. de Oliveira†, Marion Lacoue-Nègre†, Jean-François Joly†, and Ludovic Duponchel‡

† IFP Energies nouvelles, Rond-point de l'échangeur de Solaize - BP 3, 69360 Solaize, France

‡ Univ. Lille, CNRS, UMR 8516 - LASIRE – Laboratoire avancé de spectroscopie pour les interactions, la réactivité et l'environnement, 59000 Lille, France

ABSTRACT: The molecular analysis of complex matrices such as vacuum gas oils require powerful and very resolutive instruments such as Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). When a structural detail about the compounds found in these cuts is targeted, ion mobility coupled to mass spectrometry (IMMS) can be used. However, the resolving power of ion mobility is not sufficient to resolve isomers from such a complex mixture. In this paper, ion mobility-mass spectrometry coupled to separative methods such as Flash-HPLC and UHPLC has been used to characterize the neutral nitrogen compounds found in vacuum gas oils. Several vacuum gas oils obtained from several industrial processes as well as different hydrotreated samples have been analyzed through a heart-cutted HPLC-UHPLC-IM-Qq-ToF analysis to target specific compounds that have been found to be problematic to hydrotreatment thanks to ESI(-)-FT-ICR MS analyses. The extraction of the macroscopic descriptors (mobility, full-width at half-maximum) allowed to extract first trends about the samples. Then, the chromatographic peaks obtained for a given alkylation degree have been divided into several retention time segments and the corresponding mobilograms have been obtained. Bi-modal distributions have been obtained and the observed CCS and MS/MS spectra suggested the presence of compact and non-compact structures. The evolution of these structures has been followed throughout hydrotreatment to identify the most intense and less reactive groups of isomers and a difference between the quantity and the reactivity of the isomers has been found. Moreover, this methodology helped to identify whether the targeted compounds were refractory to the hydrotreatment process or reactional intermediates of the hydrotreatment process.

The characterization of complex matrices such as vacuum gas oils is a major challenge in refineries. There is a real need of eco-efficient conversion processes to convert vacuum gas oils into more valuable products. In order to improve these conversion processes, two approaches can be mentioned.

The hydrotreatment (HDT) process aims at removing impurities such as sulfur, nitrogen or metals from gas oils cuts so that they can respect the legal specifications. As these are getting more and more stringent, the hydrotreatment process needs to be more and more efficient. Despite their relatively low amount among the gas oils, the nitrogen compounds are of high concern for refiners[1]. Indeed, these compounds are known to be very problematic when undergoing hydrotreatment[2–4]. Neutral nitrogen compounds are refractory while the basic ones deactivate the catalysts used and compete with sulfur compounds for their removal[5,6]. The total nitrogen content remaining in the hydrotreated samples is a key information for assessing the efficiency of the hydrotreatment. Unfortunately, it does not provide sufficient information to understand the mechanisms involved in this process[7]. A detailed characterization of both feeds (gas oils processed by hydrotreatment) and effluents (gas oils obtained after hydrotreatment) would be very helpful to help understanding these mechanisms and thus improving the overall efficiency of hydrotreatment[8,9]. The most used method nowadays is two-dimensional comprehensive gas chromatography (GC×GC) coupled to either nitrogen chemiluminescent detector (NCD) for the absolute quantification of nitrogen compounds[10–12] or high resolution mass spectrometry (HRMS) mainly for the identification of nitrogen compounds[13,14]. However, information obtained with these methods is sometimes not sufficient to explain the reactivity differences between two feeds or to identify accurately the most refractory compounds. On the other hand, ultra-high resolution mass spectrometry (FT-ICR MS) provides an unsurpassed level of detail but the electrospray ionization source used to characterize nitrogen compounds undergoes important and complex ionization competition phenomena between the nitrogen families as well as possible different responses depending on the samples[15–17].

Thus, some approaches have already been reported in the literature combining both GC×GC quantitative features and FT-ICR MS descriptive features, but mainly for sulfur compounds and without considering both basic and neutral nitrogen compounds[18–20]. Besides, these studies were based on a small number of gas oils which is not sufficient to identify a possible matrix effect from the gas oils. In order to take into account this diesel matrix effect, the macroscopic properties of the samples can be used in multiple linear regression (MLR). This regression method has been used numerous times and is for example very useful to predict the macroscopic properties

of crude oils from NMR ^{1}H data[21,22]. Cakara et al[23] proposed an interesting MLR approach to quantify the exact amounts of Mo, Si and B in different alloys from ICP-MS measurements. The MLR models included the possible impurities in the alloys as well as isobars species which strongly helped to correct the matrix effects observed when using ICP-MS. This method might be very helpful to quantify some complex analytes while considering the matrix effect related to the analytical method used that could prevent the quantification.

This paper aims at assessing the potential of the FT-ICR MS technique as a pseudo-quantitative tool for the analysis of nitrogen compounds in gas oils by comparing the obtained concentrations to those obtained by the reference method GC×GC-NCD. As a first step, GC×GC/HRMS was used to verify the assignments of the nitrogen compounds eluted by GC×GC-NCD and to obtain blobs depending on the DBE of the compounds. A 21 gas oils database was then analyzed by GC×GC-NCD and ESI(+/-)-FT-ICR MS but the direct comparison of both methods did not highlight clear correlation between both methods. Thus, MLR modeling was used to predict the GC×GC-NCD concentrations from FT-ICR MS measurements from the different nitrogen families in a given ionization mode.

MATERIAL AND METHODS

Vacuum gas oil samples and pre-fractionation

8 different vacuum gas oils with various industrial origins were analyzed in this study: 2 Straight Run Vacuum Gas Oils (SRVGO), 1 Heavy Coker Gas Oil (HCGO), 1 Vacuum Gas Oil from Ebullating-Bed reactor (EBVGO), 3 Hydrotreated Vacuum Gas Oils (HDT) and 1 blend (MIX, 50% SRVGO + 50% EBVGO). The macroscopic properties of these samples are shown in Table S1 in Supporting Information. All samples have been pre-fractionated to remove the hydrocarbon matrix prior to UHPLC-IM-QqToF analysis. They have been pre-fractionated using a Flash HPLC 2250 chromatograph (Gilson, WI, USA), following the protocol developed by Proriol *et al*[24] after dilution of 1g in 10 mL of heptane. 5 fractions have been obtained and evaporated using nitrogen bath (about 1 bar) without heating to prevent the evaporation of light compounds.

FT-ICR MS analysis

All samples were analyzed using a LTQ FT Ultra Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS) (ThermoFisher Scientific, Bremen Germany) equipped with a 7T magnet (Oxford Instruments) and hyphenated with an ESI source (ThermoFisher Scientific) used in positive and negative modes. The chosen mass range was equal to *m/z* 98-1000. 70 scans with 4 µ-scans and their corresponding transients were recorded with an initial resolution set to 200,000 at *m/z* 300 before data processing. The ionization and ion transfer conditions for each ionization mode are described elsewhere[4]. The external mass calibration was performed using a sodium formiate clusters solution (sodium formiate provided from VWR, Fontenay-sous-Bois, France) from about 90 Da to 1000 Da.

The full data processing has been described elsewhere[4]. Phase absorption and phase correction were applied on a summed transient (sum of 70 recorded transients). The corresponding mass spectrum was then noise thresholded and peak picked by an home-made software to assign the molecular formula with the following conditions: $C_{0-50}H_{0-100}O_{0-3}N_{0-3}S_{0-3}$. The maximum content of heteroatoms in one molecular formula was set to 3 and 1 ppm of maximum mass error after mass recalibration based on N1[H] peaks. The relative intensities of the N1[H] compounds have been calculated as follows: the N1[H] peak intensity divided by the sum of intensities from all N1[H] peaks. The pseudo-concentrations are then obtained by multiplying the relative intensity times the amount of elemental neutral nitrogen (for ESI(-) data) or basic nitrogen (for ESI(+) data).

UHPLC-IM-QqToF analysis

The UHPLC separation was performed on a Acquity UPLC CSH Phenyl-Hexyl (Waters, Milford, MA, USA) of dimensions 100mm × 2.1 µm × 1.7Å. The oven temperature was 60°C and the flow rate was equal to 0.6 mL/min. The samples were diluted with Methanol (Optima LC/HRMS, ThermoFisher, Bremen, Germany) with a 50%/50% v/v ratio. The injection volume was 5 µL. A binary gradient was used with the aqueous mobile phase being ultra pure water with 0.5 mM of ammonium acetate and the organic mobile phase being 50% methanol-50% acetonitrile with 0.5 mM of ammonium acetate. A table describing the elution conditions is available in Table S1 in Supporting Information.

RESULTS AND DISCUSSION

FT-ICR/MS analysis

Usually, the blobs obtained by GC×GC-NCD are identified as a function of the nitrogen family (indoles, carbazoles, TetraHydroQuinolines [THQ], anilines...). However, the identification of the compounds when performing FT-ICR MS measurements is based on DBE. As an example, three differents blobs corresponding to tetrahydroquinolines, anilines and pyridines can be observed while only one family is considered for FT-ICR MS analysis. Moreover, the tetrahydrocarbazoles (THC) family is identified in a single blob while these compounds are identified in the Indoles family for FT-ICR/MS measurements as their DBE equal to 7 is contained between 6 and 8. Thus, in order to be able to compare the two methods, it was therefore necessary in a first step to create new blobs based on the DBE of the compounds rather than the nitrogen families.

To obtain these blobs, a GC×GC/HRMS analysis of the samples was required. However, GC×GC/HRMS is not very sensitive to nitrogen compounds when the whole gas oil sample is analyzed as only hydrocarbons are mostly detected. The gas oil samples were then pre-fractionated to extract the neutral and basic nitrogen compounds from the hydrocarbon matrix prior to GC×GC/HRMS analysis. The first two fractions contained the hydrocarbons. Three fractions containing the nitrogen compounds were obtained: one with the neutral nitrogen compounds (F3), one with some intermediate basic compounds (F4) and one with most of the basic compounds (F5). These fractions have been volume to volume mixed into a single solution called F3F4F5 to reconstruct the gas oil without the hydrocarbon matrix. An example of GC×GC/HRMS chromatogram obtained from the fractions of the GO 10 sample as well as their mixed solution F3F4F5 is shown in Figure 1. To facilitate the identification, the modulation periods and temperature gradients have been optimized for each fraction to maximize the chromatographic

space occupancy of the fractions. The mixed solutions F3F4F5 were analyzed strictly in the same conditions as GC×GC-NCD for comparisons. The identification of the molecular formula of the compounds was possible thanks to the use of HRMS and some blobs were later created based on DBE values of these compounds.

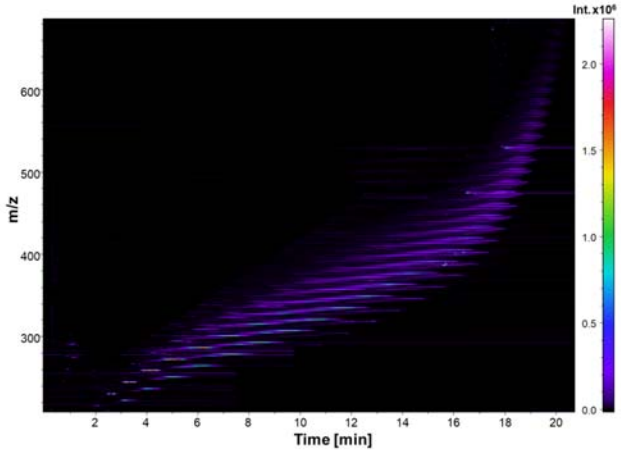

Figure 1: Heatmap obtained for the analysis of the SRVGO sample in ESI(-) mode.

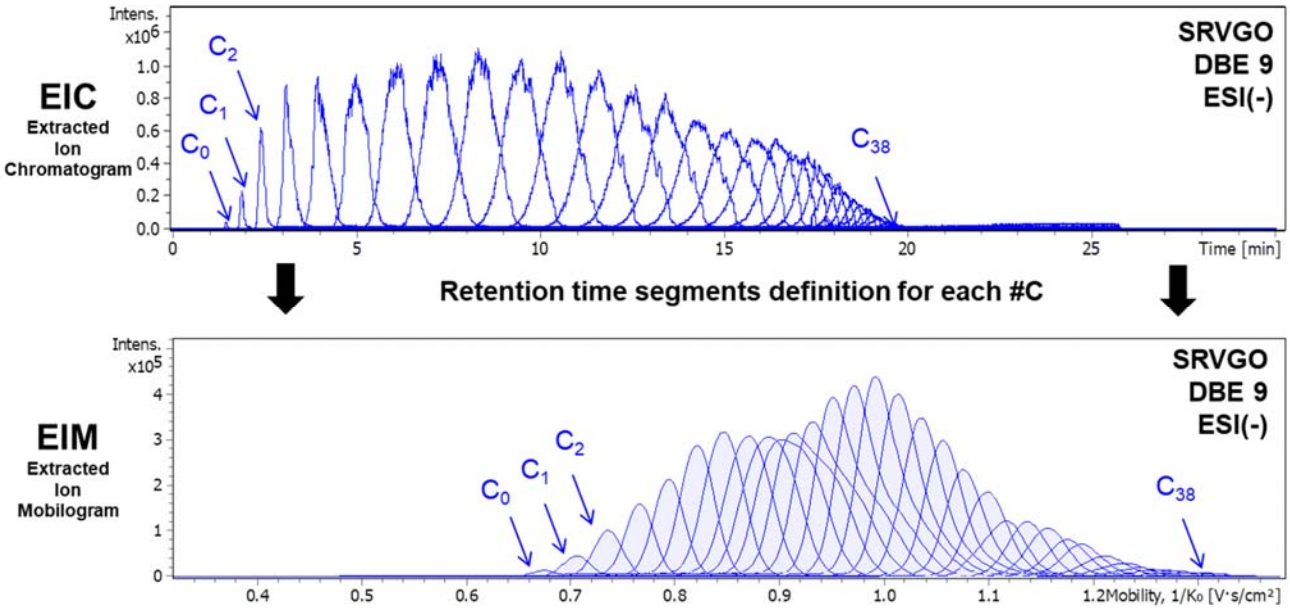

Figure 2: EIC and the corresponding EIM obtained for the DBE 9 in SRVGO sample in ESI(-) mode.

UHPLC-IM-Qq-ToF

As a first step, the GC×GC-NCD and FT-ICR MS pseudo-concentrations obtained for the 21 gas oils have been plotted for each nitrogen family. To facilitate the reading, the most abundant compounds in the DBE families have been used, such as Indoles for the family containing the neutral DBE 6-7-8 or Acridines for the family containing the basic DBE 10-11-12. These comparisons are available in Figure 3 where the different points have been colored depending on the type of gas oil of the sample. It is quite obvious that whichever family considered, no linear trend is observed between both techniques when all samples are compared. However, if we consider the points corresponding to the same type of gas oil,

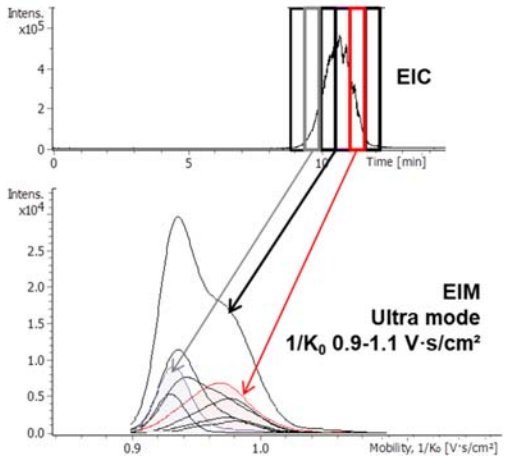

Figure 3: Extraction of the EIM depending on the retention time segment considered

some micro-trends could be identified. This confirms the strong need of a large and very diverse gas oil database to

Table 2: CCS values obtained for the DBE 10 for all samples

Sample	DBE 10, $C_{27}H_{36}N_1$	
	12.3-12.8 min	13.6-14.1 min
EBVGO	212.9 Å²	201.5 Å²
MIX	211.8 Å²	201.3 Å²
HCGO	211.9 Å²	201.7 Å²
SRVGO	212.2 Å²	200.6 Å²
HDT 1	210.6 Å²	201.3 Å²
HDT 2	212.8 Å²	200.9 Å²
HDT 3	209.2 Å²	200.4 Å²

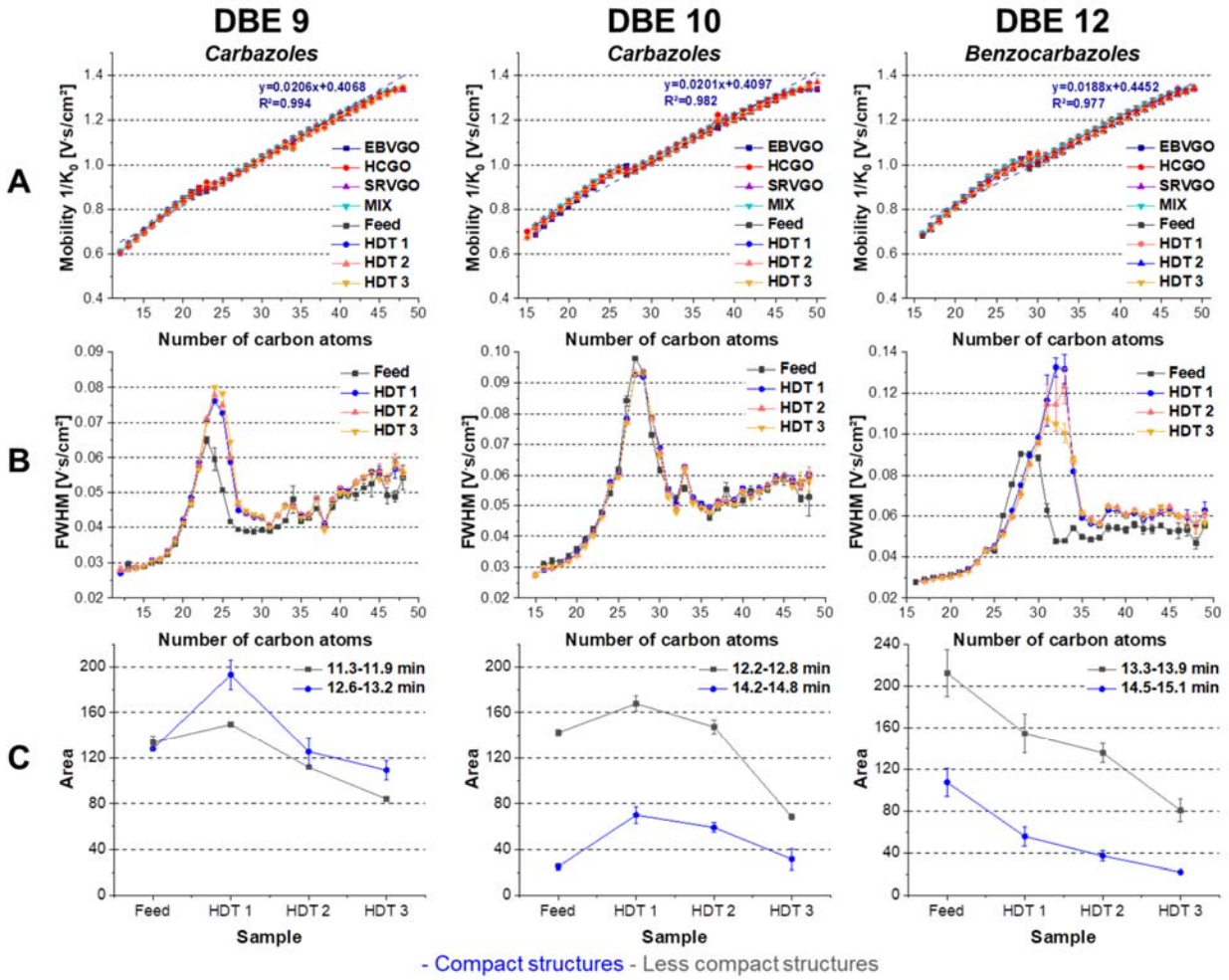

Figure 4: (A) Evolution of the mobility as a function of number of carbon atoms for the different DBE of all samples. (B) Evolution of the full-width at half-maximum (FWHM) as a function of number of carbon atoms for the different DBE of the feeds. (C) Evolution of the full-width at half-maximum (FWHM) as a function of number of carbon atoms for the different DBE of the hydrotreated samples.

MS/MS experiments.

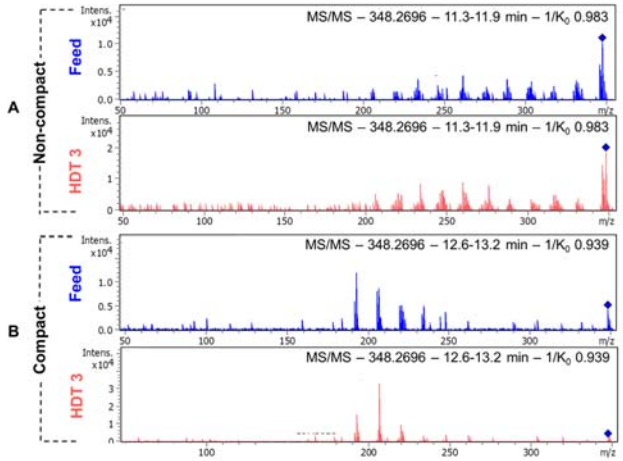

Figure 5: (A) Fragmentation spectra of $C_{25}H_{35}N_1$ compound obtained for the feed and the sample HDT 3 in non-compact configuration. (B) Fragmentation spectra obtained for the feed and the sample HDT 3 in compact configuration.

CONCLUSION

ASSOCIATED CONTENT

Supporting Information

Comparison of the F3F4F5 solutions and whole gas oils analysis in ESI(+) mode, Comparison of the F3F4F5 solutions and whole gas oils analysis in ESI(-) mode, Characteristics of MLR models (PDF).

AUTHOR INFORMATION

Corresponding Author

*alexandra.berlioz-barbier@ifpen.fr

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Alexandre Verdu from Bruker for his help in data processing. The authors would also like to thank very warmly Maëva Fieu, Sophie Hénon and Romain Comte from IFP Energies nouvelles for their help with separative methods.

REFERENCES

(1) Sau, M.; Basak, K.; Manna, U.; Santra, M.; Verma, R. P. Effects of organic nitrogen compounds on hydrotreating and hydrocracking reactions. *Catalysis Today* **2005**, *109*, 112–119.

(2) Le Maître, J.; Hubert-Roux, M.; Paupy, B.; Marceau, S.; Rüger, C. P.; Afonso, C.; Giusti, P. Structural analysis of heavy oil fractions after hydrodenitrogenation by high-resolution tandem mass spectrometry and ion mobility spectrometry. *Faraday discussions* **2019**, *218*, 417–430.

(3) Nguyen, M.T.; Pirngruber, G.; Chainet, F.; Albrieux, F.; Tayakout-Fayolle, M.; Geantet, C. Molecular level insights into straight run/coker gas oil hydrodenitrogenation by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2019,** DOI: 10.1021/acs.energyfuels.8b04432.

(4) Guillemant, J.; Albrieux, F.; Oliveira, L. P. de; Lacoue-Nègre, M.; Duponchel, L.; Joly, J.-F. Insights from Nitrogen Compounds in Gas Oils Highlighted by High-Resolution Fourier Transform Mass Spectrometry. *Analytical chemistry* **2019**, *91*, 12644–12652.

(5) Rabarihoela-Rakotovao, V.; Diehl, F.; Brunet, S. Deep HDS of Diesel Fuel: Inhibiting Effect of Nitrogen Compounds on the Transformation of the Refractory 4,6-Dimethyldibenzothiophene Over a NiMoP/Al2O3 Catalyst. *Catal Lett* **2009**, *129*, 50–60.

(6) Shin, S.; Sakanishi, K.; Mochida, I.; Grudoski, D. A.; Shinn, J. H. Identification and Reactivity of Nitrogen Molecular Species in Gas Oils. *Energy Fuels* **2000**, *14*, 539–544.

(7) López García, C.; Hudebine, D.; Schweitzer, J.-M.; Verstraete, J. J.; Ferré, D. In-depth modeling of gas oil hydrotreating: From feedstock reconstruction to reactor stability analysis. *Catalysis Today* **2010**, *150*, 279–299.

(8) Hughey, C. A.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. Elemental Composition Analysis of Processed and Unprocessed Diesel Fuel by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2001**, *15*, 1186–1193.

(9) Chen, X.; Shen, B.; Sun, J.; Wang, C.; Shan, H.; Yang, C.; Li, C. Characterization and Comparison of Nitrogen Compounds in Hydrotreated and Untreated Shale Oil by Electrospray Ionization (ESI) Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). *Energy Fuels* **2012**, *26*, 1707–1714.

(10) Yan, X. Unique selective detectors for gas chromatography: Nitrogen and sulfur chemiluminescence detectors. *J. Sep. Sci.* **2006**, *29*, 1931–1945.

(11) Adam, F.; Bertoncini, F.; Brodusch, N.; Durand, E.; Thiébaut, D.; Espinat, D.; Hennion, M.-C. New benchmark for basic and neutral nitrogen compounds speciation in middle distillates using comprehensive two-dimensional gas chromatography. *Journal of chromatography. A* **2007**, *1148*, 55–64.

(12) Chawla, B. Speciation of Nitrogen Compounds in Gasoline and Diesel Range Process Streams by Capillary Column Gas Chromatography with Chemiluminescence Detection. *Journal of Chromatographic Science* **1997**, *35*, 97–104.

(13) Mühlen, C. von; Oliveira, E. C. de; Zini, C. A.; Caramão, E. B.; Marriott, P. J. Characterization of Nitrogen-Containing Compounds in Heavy Gas Oil Petroleum Fractions Using Comprehensive Two-Dimensional Gas Chromatography Coupled to Time-of-Flight Mass Spectrometry. *Energy Fuels* **2010**, *24*, 3572–3580.

(14) Flego, C.; Zannoni, C. N-containing species in crude oil fractions: An identification and quantification method by comprehensive two-dimensional gas chromatography coupled with quadrupole mass spectrometry. *Fuel* **2011**, *90*, 2863–2869.

(15) Marshall, A. G.; Rodgers, R. P. Petroleomics: The next grand challenge for chemical analysis. *Accounts of chemical research* **2004**, *37*, 53–59.

(16) Marshall, A. G.; Rodgers, R. P. Petroleomics: Chemistry of the underworld. *PNAS*, *105*, 18090–18095.

(17) Ruddy, B. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. Positive Ion Electrospray Ionization Suppression in Petroleum and Complex Mixtures. *Energy Fuels* **2018**, *32*, 2901–2907.

(18) Adam, F.; Muller, H.; Al-Hajji, A.; Bourane, A.; Koseoglu, O. Oxidative Desulfurization Process Monitoring Using Comprehensive Two-Dimensional Gas Chromatography and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2015**, *29*, 2312–2318.

(19) Muller, H.; Adam, F. M.; Panda, S. K.; Al-Jawad, H. H.; Al-Hajji, A. A. Evaluation of quantitative sulfur speciation in gas oils by Fourier transform ion cyclotron resonance mass spectrometry: Validation by comprehensive two-dimensional gas chromatography. *Journal of the American Society for Mass Spectrometry* **2012**, *23*, 806–815.

(20) Dutriez, T.; Courtiade, M.; Ponthus, J.; Thiébaut, D.; Dulot, H.; Hennion, M.-C. Complementarity of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and high temperature comprehensive two-dimensional gas chromatography for the characterization of resin fractions from vacuum gas oils. *Fuel* **2012**, *96*, 108–119.

(21) Barbosa, L. L.; Sad, C. M.S.; Morgan, V. G.; Figueiras, P. R.; Castro, E. R.V. Application of low field NMR as an alternative technique to quantification of total acid number and sulphur content in petroleum from Brazilian reservoirs. *Fuel* **2016**, *176*, 146–152.

(22) Molina V, D.; Uribe, U. N.; Murgich, J. Correlations between SARA fractions and physicochemical properties with 1H NMR spectra of vacuum residues from Colombian crude oils. *Fuel* **2010**, *89*, 185–192.

(23) Cakara, A.; Bonta, M.; Riedl, H.; Mayrhofer, P. H.; Limbeck, A. Development of a multi-variate calibration approach for quantitative analysis of oxidation resistant Mo–Si–B coatings using laser ablation inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* **2016**, *120*, 57–62.

(24) Proriol, D.; Chahen, L. Toward New Descriptors of Basic Nitrogen Compounds in Middle Distillates by 2D NMR. *Energy Fuels* **2020**, *34*, 1347–1354.