



Supercritical fluid chromatography hyphenated with twin comprehensive two-dimensional gas chromatography for ultimate analysis of middle distillates

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ABSTRACT

This paper reports the conditions of online hyphenation of supercritical fluid chromatography (SFC) with twin comprehensive two-dimensional gas chromatography (twin-GC × GC) for detailed characterization of middle distillates; this is essential for a better understanding of reactions involved in refining processes. In this configuration, saturated and unsaturated compounds that have been fractionated by SFC are transferred on two different GC × GC columns sets (twin-GC × GC) placed in the same GC oven. Cryogenic focusing is used for transfer of fractions into the first dimension columns before simultaneous GC × GC analysis of both saturated and unsaturated fractions. The benefits of SFC–twin-GC × GC are demonstrated for the extended alkane, iso-alkane, alkene, naphthenes and aromatics analysis (so-called PIONA analysis) of diesel samples which can be achieved in one single injection. For that purpose, saturated and unsaturated compounds have been separated by SFC using a silver loaded silica column prior to GC × GC analysis. Alkenes and naphthenes are quantitatively recovered in the unsaturated and saturated fractions, respectively, allowing their identification in various diesel samples. Thus, resolution between each class of compounds is significantly improved compared to a single GC × GC run, and for the first time, an extended PIONA analysis of diesel samples is presented.

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1. Introduction

In order to better understand and improve conversion processes [1] involved in the production of diesel fuels (C₁₃–C₂₅), there is a strong need for detailed molecular characterization of feed stocks and resulting products. Typical petrochemical samples in the middle distillate range may contain several hundreds of thousands of compounds [2] that is why one-dimensional separation techniques cannot separate all these compounds [3]. For instance, high-resolution gas chromatography (HRGC) only allows for the complete separation of products having constituents up to C9 for straight run distillates and even less for more complex mixtures containing alkenes [4].

The recent introduction of comprehensive two-dimensional gas chromatography (GC × GC) opened up new perspective to achieve the detailed hydrocarbon analysis (DHA) of middle distillates. Indeed, owing to a higher resolution power [5,6] and an enhanced

sensitivity [4,7], comprehensive two-dimensional gas chromatography offers unsurpassed possibilities for the characterization of petroleum products [8–10]. Still, GC × GC fails at discriminating all classes of hydrocarbons in middle distillates: alkenes and polycyclic naphthenes coelute with mononaphthenes and monoaromatics, respectively, which prevents the DHA. This lack of resolution clearly demonstrates that the dimensionality of the samples [6], that is the number of separation dimensions required to separate hydrocarbons contained in middle distillates, exceeds the number of separation dimensions of GC × GC and that an additional separation dimension is needed to fully characterize middle distillates.

It was recently shown that gas phase fractionation into saturated and unsaturated compounds using a silver(I) impregnated silica trap prior to GC × GC is successful in the C₈–C₁₅ range [11]. However, thermodynamic study of the sorption of unsaturated compounds on this trap revealed that hydrocarbons having more 15 atoms of carbons cannot be removed from the trap without being thermally cracked. Therefore, additional separation mechanisms involving a dense phase rather than a gas phase were investigated in order to extend the use of GC × GC towards heavier cuts. Off-line HPLC fractionation into saturated and unsaturated compounds was also successfully applied to the characterization of middle distillates [12,13]. Edam demonstrated the benefits of fractionating

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the saturated and the aromatic compounds from each other; nevertheless, owing to of the fractionation step, alkenes remained coeluted with the aliphatic hydrocarbons. While implementing a silver loaded silica column, Mao et al. [13] achieved the HPLC separation of saturated and unsaturated hydrocarbons in the form of two narrow peaks that have been collected and reinjected in GC \times GC to achieve the first PIONA analysis of middle distillates. However, in this late case, the selected GC \times GC separation conditions did not allow for the identification and quantification of the different classes of naphthenes.

Off-line multiple-stage techniques are susceptible to solute loss and contamination during intermediate collection and reconcentration steps [14]. This is the reason why online coupling of the HPLC and GC \times GC analytical stages is highly desirable. However, the large volumes resulting from the HPLC separation are unsuitable for direct transfer to GC; special interfaces (retention gap, solvent evaporation) likely to remove the HPLC solvent need to be implemented for online hyphenation of HPLC to GC [15]. In this study, supercritical fluid chromatography (SFC) was preferred to HPLC with regard to easier online hyphenation to GC \times GC. Indeed, hydrocarbon group type separation achieved with supercritical fluids have been proven to provide similar resolution and faster separation than liquid chromatography due to liquid like properties while keeping gas like viscosity [16–18]. Further, a simple decompression of supercritical fluid through a restrictor directly placed into a capillary gas chromatographic injection port allows the transfer from the dense phase to the gas phase, thus removal of supercritical fluid can be easily achieved without any solvent evaporation or any complex procedure prior to GC analysis [19,20].

In order to achieve the separation of hydrocarbons by chemical class (alkane, iso-alkane, alkene, naphthenes and aromatics) and by carbon number, so-called extended PIONA analysis, fully automated and online hyphenation of SFC to a twin-GC \times GC device is described. The first part of this paper deals with the evaluation of SFC chromatographic conditions to achieve a separation of middle distillates into saturated and unsaturated fractions. In the second part, the conditions of online hyphenation of SFC to a twin-GC \times GC device are described. In a third part, a SFC–twin-GC \times GC procedure (both qualitative and quantitative) to unravel the composition of middle distillates is proposed and discussed in depth. Finally, the benefits of SFC–twin-GC \times GC system are demonstrated for the extended PIONA of a diesel sample.

2. Experimental

2.1. Chemicals

Analytical gases were provided by Air Liquide (Feyzin, France) at a minimum purity of 99.999%. Solvents of HPLC grade were purchased from Sigma–Aldrich (St. Quentin Fallavier, France). Two diesel cuts were provided by IFP–Lyon and were obtained from cracking processes. LCO diesel (density: 0.941; total sulphur content: 1.56%; boiling points range: 140–429 °C) referred to as Light Cycle Oil diesel. COK diesel (density: 0.873; total sulphur content: 2.93%; boiling points range: 175–353 °C) referred to as cokefaction diesel.

A complete hydrocarbon standard mixture (STD1), representative of all hydrocarbons families occurring in common diesel samples was prepared (i) to check the ability of the SFC system to separate saturated and unsaturated hydrocarbons from each other and (ii) to evaluate the ability of the interface to quantitatively handle both saturated and unsaturated hydrocarbons. STD1 composition is reported in Table 2. A second hydrocarbon standard mixture (STD2) consisting in tertibutylcyclohexane, *n*-decane, indane and indene was prepared in order to evaluate

the cryofocussing capabilities of the developed interface. Analyte's concentrations in STD1 and STD2 ranged between and 0.03 and 0.05 wt%. Hydrocarbons were purchased at Chiron (Trondheim, Norway).

2.2. SFC fractionation

Separation of saturated and unsaturated fractions was performed using SFC. A diagram of the system is shown in Fig. 1A. The SFC column was installed in the oven of a 5890 gas chromatograph (Agilent Technologies, Massy, France) to ensure a constant temperature during separation. The separation was carried out in the downstream mode [21] for independent control of flow rate and pressure in the column. Mobile phase (carbon dioxide) was delivered by a model 306 pump (Gilson, France) at constant flow. Pressure and flow control was achieved using a module 821 (Gilson, France). To avoid column saturation 5 μ L of sample diluted in CS₂ (1:3, v/v) were injected using a 6 ports Valco valve (Fig. 1A, valve no. 1). The SFC column was connected to a 6 ports valve (Fig. 1A, valve no. 2) in order to be operated either in foreflush or backflush modes. A third valve (Fig. 1A, valve no. 3) was used to sequentially direct the SFC effluent to two different integral restrictors [22] calibrated at 15 mL/min while controlling the backpressure with the pressure regulator placed in downstream. For that purpose, valve no. 3 was connected to two low dead volume T-connectors. One side of each T-connector was connected to valve no. 3 for backpressure control using the module 821. On the other side of each T-connector, one integral restrictor made from deactivated fused silica tubing (50 μ m I.D.) was connected to a flame ionisation detector (FID) for SFC separation monitoring. The selection of one or the other restrictor was obtained by actuating the valve no. 3. Valve no. 3 remained in the off position during SFC monitoring and optimisation. For a better reproducibility, valves control and FID signal monitoring were achieved using the GC Chemstation.

Both a hydrocarbon group type separation column (LiChrosphere Si 60, 250 mm \times 4.6 mm, 5 μ m particle diameter, Merck, Germany) and a silver loaded column (Chromosphere lipids, 100 mm \times 4.6 mm, Varian, Courtaboeuf, France) have been investigated.

2.3. GC and GC \times GC methods

The GC system consisted in a modified gas chromatograph 6890N (Agilent Technologies, Massy, France). In this work, the GC was equipped with two split/splitless injectors and two FID systems in order to allow the simultaneous analysis of both saturated and unsaturated fractions on two different column sets. In this configuration (twin-GC), both saturated and unsaturated fractions were separated on a non-polar column (PONA, polydimethylsiloxane, Agilent Technologies, Massy, France, 15 m, 0.2 mm, 0.5 μ m). The separation was carried out at a constant flow of 0.9 mL/min. FID systems set at 320 °C were used for detection. H₂, air and He (make up) flows were, respectively, 35, 400 and 25 mL/min. When the instrument was used in the twin-GC \times GC mode, a dual stage carbon dioxide jet modulator built in house as described by Beens et al. [23] was used and modulation was set at 12 s. The choice of the operating conditions (oven temperature program and column) for both the saturated and the unsaturated fractions is presented in Section 3. The two secondary columns were fixed using two-holes ferrules (Varian, France) on the modulator support. In order to avoid vibrations of the columns, a septum was placed between the two carbon dioxide jets to hold the two columns together. After acquisition, signal was exported as a CSV-file from the Chemstation for data handling. Contour plotting, GC \times GC peak collection, retention time measurements, peak integration and report have been done using the 2D-ChromTM software developed in our laboratory; this

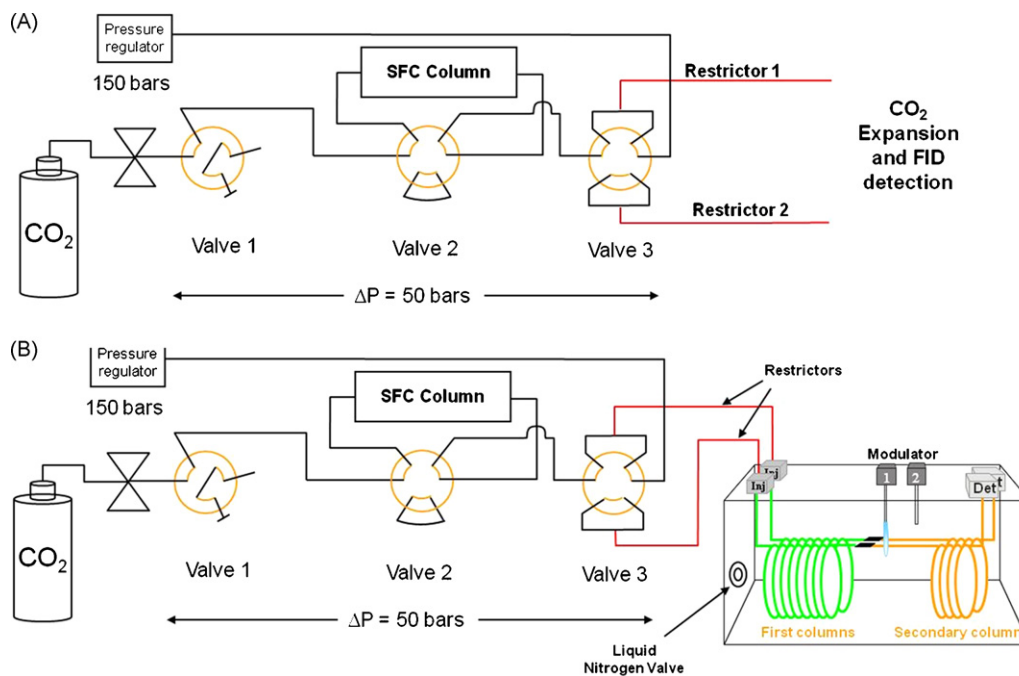


Fig. 1. (A) Valve diagram of SFC system used for group type separation. (B) Valve diagram of SFC-twin-GC \times GC for extensive group type analysis of middle distillates.

software features featuring automatic peak finding and blob fitting in order to improve reproducibility and accuracy of integration.

2.4. Hyphenation of SFC and GC

SFC was used as a fractionation step prior to GC (respectively GC \times GC) analysis. In this respect the SFC effluent (Fig. 1B) was transferred to split/splitless injector through the restrictors which were directly inserted in the septa of the GC injectors (the length of the restrictor inserted in the liner is discussed in Section 3). Injectors were operated in the splitless mode. In order to avoid precipitation of analytes in the injector during CO₂ depressurization [24] and improve their transfer to the GC column, GC injectors were heated at 320 °C and the split purges were closed during sample transfer. To reduce injection band width during sample transfer, analytes were cryogenically focused (trapping conditions are discussed in Section 3) using liquid nitrogen dispensed to the GC oven via a valve (Agilent, France). Then GC oven temperature was increased up to 40 °C at a rate of 20 °C/min and from 40 to 300 °C at a rate of 2 °C/min. Based on the analysis of test compounds (STD1, see Section 2.4 for composition), it was found that in this configuration, the injection of 5 μ L diesel samples in the SFC-GC system roughly corresponded to the direct split injection of 0.5 μ L diesel samples in the GC system (split ratio of 1/100). Thus, even though most of the SFC flow is split towards the pressure regulator, one can consider that under the chosen SFC-GC \times GC operating conditions, the same amount of sample is transferred from the SFC to the GC as under direct injection conditions, that is the injection of 0.5 μ L of sample using a 1/100 split ratio.

2.5. Regular GC simulated distillation (GC SimDis)

Simulated distillation analysis was achieved using a HP 6890 chromatograph (Agilent Technologies, Massy, France) equipped with a FID system and a cool on-column inlet. Analysis was carried out at a constant helium flow of 10 mL/min on a MXT-1 (Restek, France) Silcosteel[®]-treated stainless steel capillary column (15 m \times 0.53 mm \times 0.5 μ m) which was heated from 35 °C (hold 1 min) to 390 °C at a rate of 10 °C/min. Detector temperature was

set at 400 °C. The SimDis curve was obtained by using the algorithm defined in the ASTM D-2887 [25] method. Calculation was performed using the Chromdis software (Gecil Process, France).

3. Results

3.1. SFC separation

In this work, SFC is used as a pre-separation step of saturated and unsaturated compounds contained in middle distillates prior to their separate analysis. Therefore, the first step of this study consisted in the characterization of the SFC separation. For that purpose, a complete hydrocarbon mixture (STD1), representative of all hydrocarbon families occurring in middle distillates was subjected to SFC analysis to evaluate its ability to quantitatively separate saturated and unsaturated hydrocarbons from each other. Experimental conditions corresponded to those reported in Section 2.2.

In the case of the silica column, the saturated fraction was eluted in the fore flush mode within 2.2 min. Then the silica column was operated in the backflush mode during 8 min to elute aromatic compounds. In this manner, aromatics could be eluted as a single peak within 8 min instead of 15 min in the foreflush mode. In this part of the study, saturated and unsaturated compounds are sent to the same GC column. However, one should note that to send saturated and unsaturated fractions onto two different GC column sets, valve no. 3 would need to be activated ca. 20 s after backflush in order to purge the first restrictor. Indeed, as demonstrated in the literature, the silica column does not lead to baseline separation of saturated and unsaturated hydrocarbons, meaning that unless restrictor is purged, analytes contained in this one would be lost.

In the case of the silver loaded cation exchange column, the saturated compounds were eluted in the foreflush mode within 3.5 min. As suggested by Anderson et al. [16], the unsaturated compounds (aromatics and alkenes) were then backflushed from the SFC column during 35 min until desorption of unsaturated hydrocarbons was completed while acting valve no. 3. In contrary to the silica one, the silver loaded cation exchange column allowed a baseline separation of saturated and unsaturated hydrocarbons. Thus, if both fractions needed to be sent to two different GC columns, valves

Table 1
Main properties of studied diesel samples.

	LCO diesel	COK diesel
Density at 15 °C (g/cm ³)	0.9415	0.873
Total sulphur (% S)	1.56	2.93
Boiling point interval (°C)	140–429	175–373

no. 2 and no. 3 could be activated simultaneously without risk of analyte loss.

In order to evaluate the ability of the SFC columns to handle quantitatively both saturated and unsaturated hydrocarbons separately, the chromatograms obtained for STD1 mixture through the interface have been integrated. Results are reported in Table 1.

From a quantitative point of view, the SFC results were in good agreement with theoretical results. As suggested in the literature [16,26], discrepancies between silica gel and silver loaded cation exchange SFC columns can be attributed to the presence of alkenes which were eluted in the saturated fraction when the silica column was used, whereas they were recovered in the so-called aromatic fraction when the silver loaded cation exchange column was used. These results underline the limitations of the silica column which failed to discriminate alkenes from saturated compounds. In practice the silver loaded cation exchange column provided analyst with the saturated and unsaturated ratio whereas the silica column only allowed the determination of the saturated and alkene to aromatic ratio. For these reasons, the silver loaded cation exchange column was selected for the analysis of middle distillates.

3.2. SFC–GC hyphenation

Parameters likely to play a key role on the transfer of analytes from SFC to GC (respectively GC × GC) or on the quality of the GC separation were studied. These parameters included (i) the GC liner shape, (ii) the length of the restrictor in the GC liner, (iii) the restrictor flow rate and (iv) the impact of the cryofocussing temperature. Even though quantitative aspects are discussed later (see Section 3.3), results reported in Table 3 were used as reference values to study the impact of these parameters on the recovery yields.

3.2.1. Shape of the GC liner

In order to investigate the impact of the shape of the GC inlet liner on our system, experimental setup reported in Section 2.3 was used. Straight, single gooseneck and double gooseneck liners were implemented to the SFC–twin–GC × GC device for the analysis of STD1 mixture. Double gooseneck liners were found to have a significant impact on the operation of the system. Indeed, they were responsible for a high overpressure in the injector which caused a shut down of the instrument. When straight or single gooseneck inlet liners were used, no overpressure could be reported. Further, the analysis of STD1 mixture using those two liners showed excellent yields of recoveries (between 94 and 113%).

3.2.2. Length of the restrictor in the GC liner

The position of the restrictor in the GC liner was also investigated. For that purpose, the restrictor was introduced at different length (2, 4 and 6 cm) in the GC liner. Otherwise, experimental setup and operating conditions corresponded to those reported in Section 2.3. Yields of recoveries were evaluated for each compounds contained in STD1 mixture in each configuration. Restrictor depth was not found to affect yields of recoveries. Consequently, analyses were carried out using a restrictor introduced at 4 cm in the liner of GC injector, as described in the literature by Levy et al. [20].

3.2.3. Restrictor flow rate

The impact of restrictor flow rate was studied. In this respect, several restrictors were calibrated to deliver 7.5, 15 and 25 mL/min and implemented to our SFC–twin–GC (experimental setup as in Section 2.2) system. Yields of recovery using the three restrictors were evaluated for each compound contained in STD1 mixture. The part of GC-chromatograms corresponding to the elution of normal-octadecane using the three restrictors are superimposed in Fig. 2.

As can be seen, the higher the restrictor flow rate, the wider the peak at the baseline. Further to the fronting, increasing the CO₂ flow rate in the restrictor was found to deform peak (shown with a circle in Fig. 2A). Since the increase in CO₂ flow is correlated with an increase in the amount of material transferred from the SFC to the GC column, the peak deformation observed on the chromatogram suggests a possible overloading of the GC column. In addition, as shown in Fig. 2A, *n*-octadecane peak started around 73 min when the 20 mL/min restrictor was implemented. In contrary, the same compound started to elute around 73.4 min when restrictors calibrated at smaller flows were used. Eventhough this peak deformation was negligible in the case of one-dimensional chromatograms (1D-chromatograms), it was found to have a significant effect on the two-dimensional chromatograms. This phenomenon resulted in a strong peak fronting of the *n*-alkanes which are also the most concentrated compounds in middle distillates (shown in Fig. 2B with red circles). This observation seems to confirm overloading of the GC column when high CO₂ restrictor flow rates were used. Despite the peak deformation observed for the 20 mL/min restrictor, yields of recoveries obtained for STD1 compounds were comparable to those measured at lower flow rates. Therefore, in order to conduct a quantitative study, transfer of analytes was achieved using restrictor having a maximum flow rate of 15 mL/min.

3.2.4. Impact of cryofocussing temperature on GC separation

In the SFC–twin–GC (respectively SFC–twin–GC × GC) configuration, analytes continuously transferred from SFC to GC had to be trapped on the head of the GC column until SFC separation was completed. As suggested by Venter and Rohwer [19,27], cryogenic trapping (cryofocussing) of solutes was chosen and the effect of trapping temperature on the gas chromatographic profile was investigated. In this respect, a standard mixture (STD2) containing two most volatile saturated and two most volatile aromatic hydrocarbons contained in STD1 mixture (i.e. compounds that were the most likely to be poorly focused) occurring in middle distillates was submitted to the SFC separation before being transferred from SFC to GC as described in Section 2.3. Until completion of the SFC separation, trapping of analytes was performed at different temperatures (+30, 0, –20 and –50 °C) on the head of the GC column. Afterwards, GC analysis was started and resolution between saturated and unsaturated hydrocarbons on the GC column was evaluated. Experiments were carried out with the silver column using the SFC conditions determined in Section 2.3. For comparison purposes, reference resolution values were obtained by direct injection of the standard mixture in the GC system in the split mode (split ratio was set at 100). In this case, the oven was programmed from 50 to 300 °C at a rate of 2 °C/min. Results are reported in Table 2.

As can be seen in Table 2, in the case of saturated compounds, the resolution was greater than reference value for trapping temperatures below 0 °C, indicating that this temperature would be sufficient to trap properly saturated compounds. In contrary, the resolution between unsaturated compounds was more affected by trapping temperature. For instance, at 30 and 0 °C, no resolution values were obtained using the silver loaded cation exchange column whereas these compounds were fully resolved when focussed

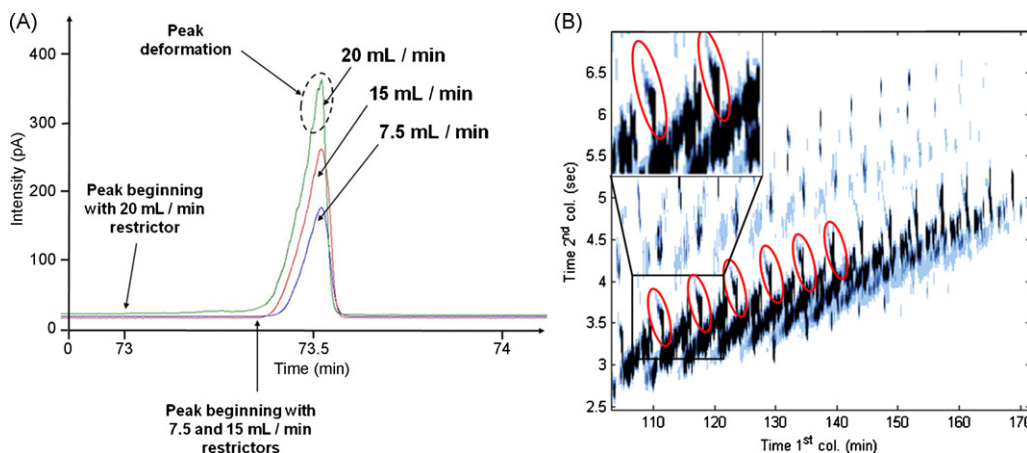


Fig. 2. Illustration of the impact of the restrictor flow rate on the peak shape of *n*-octadecane on 1D-chromatogram (A) and consequences on the 2D-chromatogram of a diesel sample obtained with a 20 mL/min restrictor flow rate (B). Conditions as in Section 3.2.3.

at -50°C . Measured resolution values equaled the reference values at this temperature, indicating that cryofocussing needed to be achieved at -50°C . Attempts to trap analytes at temperatures below -80°C remained unsuccessful: analytes could not be detected. Below -60°C , the GC column was operated out of its recommended operating conditions (minimal operating temperature of the stationary phase is -60°C); a phase transition could be responsible for poor results observed. Since CO_2 expansion occurred in the heated liner (320°C) of the gas chromatograph, the formation of a frozen plug [28] resulting from the CO_2 expansion in the GC liner was also rejected. For these reasons, trapping at -50°C was used in this study.

3.3. SFC–twin-GC \times GC approach

3.3.1. Retention and separation of analytes in GC \times GC

One of the goals of this work deals with the simultaneous identification and quantification of saturated and unsaturated hydrocarbons occurring in middle distillates. The GC \times GC analysis usually implies the hyphenation of a first non-polar column (polydimethylsiloxane phase) which enables the separation of analytes according to their volatility (i.e. by carbon number) and a short second polar column (phenylsiloxane phase) to elute compounds according to the number of aromatic rings [8,29]. From a chromatographic point of view, the SFC fractionation of the samples prior to GC \times GC implies the reduction of the number of hydrocarbon groups in the fractions that have to be analysed in GC \times GC. More chromatographic space, especially according to the second dimension, should be available for the analysis of each fraction of interest; consequently GC \times GC chromatographic conditions could be adapted to take advantage of this extended separation space. Therefore a conventional first non-polar column (PONA, 15 m \times 0.20 mm I.D., 1.0 μm) was used for both saturated and unsaturated fractions and our efforts have mainly been focussed on the choice of the second dimension columns (column length, film thickness) as well as on the oven program.

Table 2

Evaluation of SFC for the determination of the saturated to unsaturated ratio of STD1 mixture (results are expressed in wt%).

	SFC (Si)	SFC (Ag)	Theoretical distribution
Saturated	40.9	31.7	30.0
Aromatics	59.1	68.3	58.0
Olefins	–	–	12.0

3.3.1.1. Choice of the second dimension column for the saturated fraction. In a first setup, the impact of the secondary column length as well as the temperature gradient on the separation of the saturated hydrocarbons was investigated. Purposely, STD1 mixture was subjected to SFC–twin-GC \times GC. Experiments were conducted using two oven temperature ramps (2 and $4^{\circ}\text{C}/\text{min}$) and for each gradient two secondary column having different length (2.0 and 4.0 m) were tested. The film thickness (0.1 μm) and the nature of the stationary phase (BPX 50) were kept constant. The modulation period was 12 s. Corresponding 2D-chromatograms are reported in Fig. 3A and B.

As expected, the implementation of a longer column allowed a better separation of saturated compounds according to the second dimension. For instance, the resolution between compounds 26 and 27 is increased from 3.2 to 7.2 when the secondary column is increased from 2.0 to 4.0 m. The improvement of the separation is consistent with an increase in the peak capacity of the considered GC \times GC system. For instance, alkanes and dinaphthenes compounds were separated over 6 s and some free chromatographic space remained available for polycyclic naphthenes occurring in hydrotreated products [12,29] when a 4 m long secondary column and a $2^{\circ}\text{C}/\text{min}$ GC temperature gradient were used. Comparison of Fig. 3A and B also demonstrates a better spreading of the peaks on the chromatographic space when a low temperature ramp was used. For instance, decaline (Fig. 3, no. 27) eluted at 4 and 6 s on the 4.0 m long secondary column when 2 and $4^{\circ}\text{C}/\text{min}$ temperature gradients were used, respectively. For these reasons, the separation of the saturated compounds was carried out on a 4.0 m long secondary column using a $2^{\circ}\text{C}/\text{min}$ temperature gradient. A modification of the first dimension retention times when the second dimension length was modified is also worth noticing: owing to an increase of pressure drop within the second dimension, the retention times in the first dimension were longer when the 4 m secondary column was implemented [9].

3.3.1.2. Choice of the second dimension for the separation of the unsaturated fraction. In this respect, STD1 mixture was subjected to SFC–twin-GC \times GC analysis. Experiments were carried out using two different column lengths (1.6 and 2.6 m), and for each column length, two film thickness (0.1 and 0.2 μm). The nature of the stationary phase (BPX 50), the internal diameter (0.1 mm), the modulation period (12 s) and the oven program ($2^{\circ}\text{C}/\text{min}$) were kept constant. Corresponding 2D-chromatograms are reported in Fig. 3C and D.

A phenylic (50% phenylsiloxane–50% polydimethylsiloxane) column was implemented as it has been demonstrated in the litera-

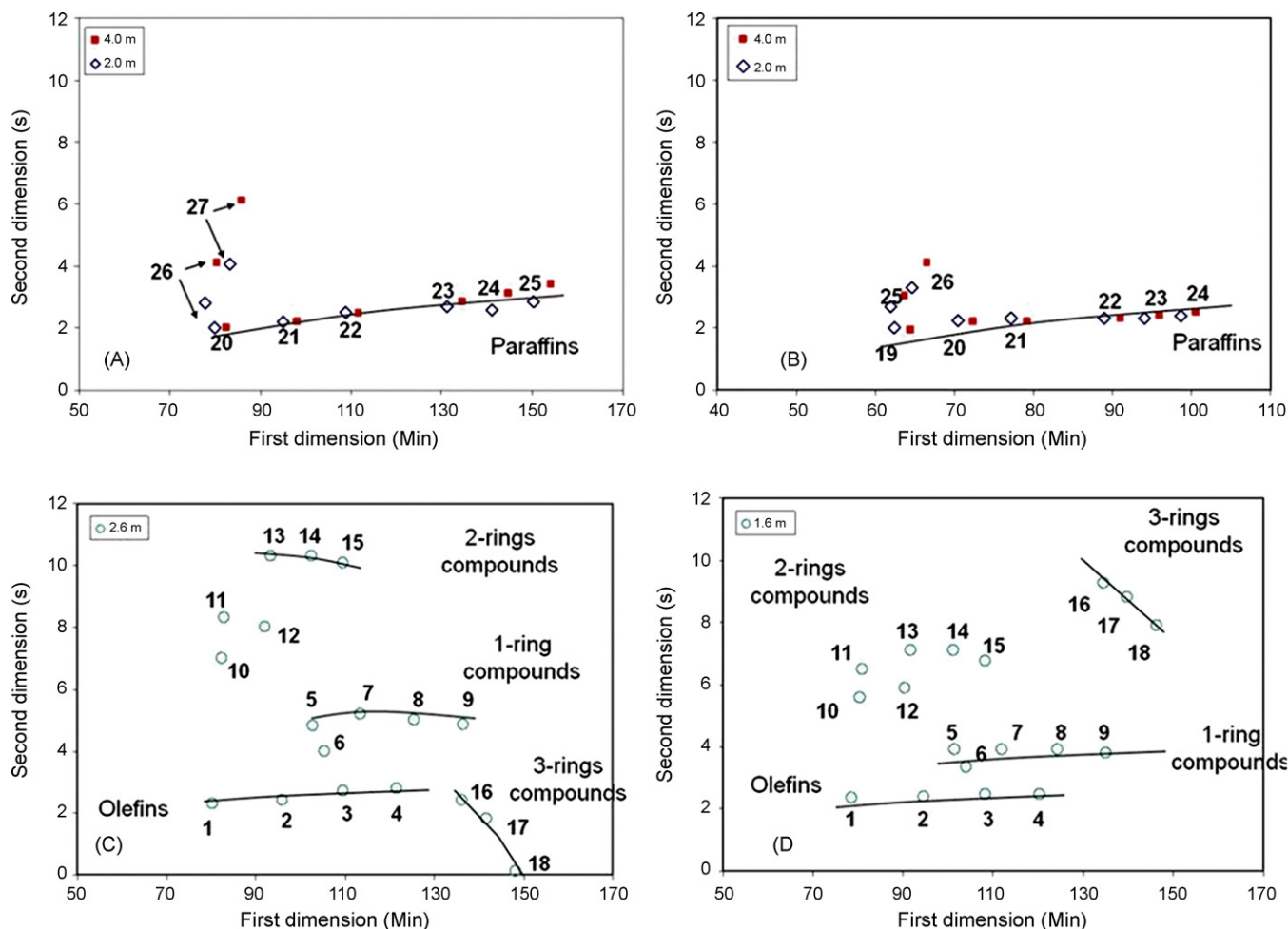


Fig. 3. Impact of the secondary column dimension on the separation of compounds contained in STD1: 2D-plot of peak apices of after SFC–twin-GC × GC analysis. Impact of the column length (2.0 or 4.0 m) using a 2 °C/min (A) and a 4 °C/min (B) oven program on the saturated compounds contained in STD1. Impact of the column length (1.6 m, C or 2.6 m, D) on the separation of peak apices of unsaturated compounds contained in STD1 after SFC–twin-GC × GC using a 2 °C/min oven program. Other conditions as in Sections 2.2 and 2.3.

ture that it is well adapted for the analysis of aromatic compounds; therefore, efforts were mainly focused on the choice of its length and film thickness. Indeed, since the GC oven and the modulation system were common to the GC × GC columns sets used for the analysis of both saturated and unsaturated compounds, the oven temperature program have been already determined based on the analysis of the saturated fraction.

Data reported in Fig. 3 clearly show a good peak spreading of analytes on chromatographic space but a significant wrap around of three ring aromatic compounds occurs when a 2.6 m long secondary column having a 0.1 μm stationary phase film thickness was implemented. For this reason, the 1.6 m long secondary column having a 0.1 μm stationary phase film thickness was preferred to the 2.6 m long column.

Impact of the film thickness was also investigated. An increase in the film thickness from 0.1 to 0.2 μm, even using a 1.6 m long column systematically resulted in wrap around of triaromatics (results not shown), therefore the analysis of the unsaturated fraction has been conducted using a 1.6 m BPX 50 column having a 0.1 mm film thickness.

3.3.2. Description of the quantitative procedure

For quantification purpose, the area of each class of compounds was initially determined in each fraction (saturated and unsaturated). To obtain relative concentration of each class of compounds

in the sample of origin, the corrected areas were balanced by the saturated/unsaturated ratio which was obtained using setup described in Fig. 1. For instance, content of family j in the full diesel sample (C_j) was obtained from the content of family j initially present in fraction i ($C_{i,j}$) using Eq. (1) where fc_i corresponds to the relative weight percentage of fraction i (saturated or unsaturated) in the considered diesel:

$$C_j = fc_i \times C_{i,j} \quad (1)$$

One should note, that in this study, the saturated/unsaturated ratio was determined by injection of sample in conditions described in Section 2.1. However, for routine analysis, one could consider the implementation of a third FID system between valve no. 3 and the pressure regulator for direct acquisition of the saturated/unsaturated balance.

3.3.3. Evaluation of the SFC–twin-GC × GC quantitation procedure

In order to evaluate the ability of the SFC–twin-GC × GC system for quantitative purposes, 2D-chromatograms obtained for STD1 (Fig. 3A and D) have been integrated. Results are shown in Table 3 for the silver loaded cation exchange SFC column. RSD was evaluated on the basis of five replicates and was found to be 12% within a 99% confidence interval. From a quantitative point of view, the yields of recovery of both fractions ranged between 93 and 112%. Alkenes were also quantitatively recovered (recovery yields ranged

Table 3
Effect of trapping temperature on the resolution of test compounds. Experimental setup and operating conditions as in Sections 2.2 and 2.3. Reference resolution values (ref.) were obtained by direct injection in GC (see text for details).

Temperature (°C)	Resolution of saturated compounds (tertiobutylcyclohexane/ <i>n</i> C10)			Resolution of unsaturated compounds (indene/indane)		
	Silica column	Silver column	Ref.	Silica column	Silver column ^a	Ref.
30	9.29	6.81		1.42	–	
0	14.17	11.57	10.17	2.03	–	2.42
–20	12.35	10.67		2.15	1.90	
–50	13.54	11.04		2.67	2.31	

^a No resolution values could be reported for the silver loaded cation exchange column at 0 and 30 °C.

between 95 and 107%) in the expected fraction. These results also underline that the operating conditions (switching time, trapping conditions) were correctly selected and validate the approach chosen.

3.3.4. Impact of the fractionation step on the hydrocarbon distribution

In order to make sure that the fractionation procedure did not modify the distribution of hydrocarbons, in particular at the expense of volatile compounds, the reconstructed simulated distillation curves obtained for LCO diesel has been compared to the simulated distillation curves of the non-fractionated diesel sample obtained from the standardized method ASTM D-2887 [25] as described in Section 2.5. Purposely, simulated distillation curves of each fraction (saturated and unsaturated fractions) were reconstructed using GC × GC data obtained for group type analysis (Fig. 5). Elution zone was divided into slices. The retention time (RT) of the slice was converted into a boiling point using a relationship established between RT and boiling points of standard compounds (alkanes and 1-alkenes for the saturated and unsaturated fractions, respectively). For each fraction, the area was converted into a cumulated wt% to yield a distillation curve. The two simulated distillation curves were then balanced by the saturated to unsaturated ratio (Eq. (1)) and summed before being normalized to provide the reconstructed simulated distillation (SimDist) curve (GC × GC SimDist curve) of the fractionated diesel sample. The comparison of reference and reconstructed simulated distillation curves is proposed in Fig. 4.

Fig. 4 shows that the difference between the reconstructed and reference simulated distillation curves does not exceed 5 °C in the range 5–95% and 7 °C for amounts outside this range, indicating, according to ASTM D-2887 [25] reference method, that there was no modification of the distribution of hydrocarbons when the diesel samples was subjected to the SFC fractionation procedure. These results also indicate that all compounds eluted from the SFC column and were subjected to the GC × GC separation, which confirms the good quantitative results. Therefore, this procedure was applied to

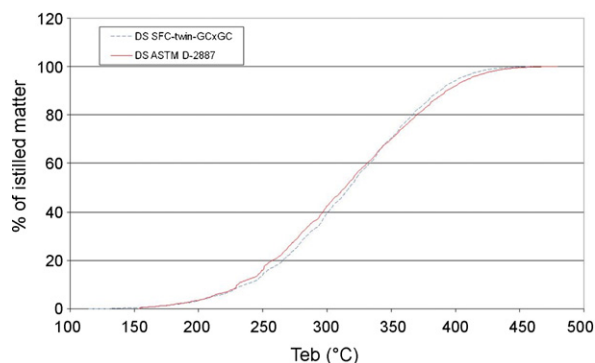


Fig. 4. Comparison of reference and SFC-twin-GC × GC reconstructed simulated distillation curves for cokefaction diesel.

two complex diesel samples for identification purposes and precise quantitative analysis.

3.4. Application to the PIONA analysis of diesel samples

3.4.1. Qualitative study/identification of compounds

Developed chromatographic conditions described in previous sections was applied to the analysis of two diesel selected for their high alkene content as well as for the presence of polycyclic naphthenes. The two-dimensional chromatograms obtained for LCO and COK diesel samples are presented in Fig. 5. The assignment of hydrocarbons is based on retention times of standard compounds.

As shown in Fig. 5, SFC-twin-GC × GC enabled the separation of hydrocarbons occurring in diesel samples into saturated and unsaturated compounds. The unsaturated compounds included alkanes (P), mononaphthenes (MN), dinaphthenes (DN) and trinaphthene (TN) which are usually coeluting with monoaromatics when GC × GC analysis was carried out without SFC fractionation. The unsaturated compounds included alkenes (O), monoaromatics (MA), diaromatics (DA) and triaromatics (TA).

The increased peak capacity offered by our SFC-twin-GC × GC system also enabled a deeper insight into the composition of the saturated and unsaturated fractions, resulting in the identification of typical structures. Each class of compounds could be divided into subbands corresponding to groups of isomers [30], meaning that the extended PIONA analysis could be determined [30]. In the case of the saturated fraction, at a given number of atoms of carbon, a clear distinction could be done between the *n*-alkylcyclohexane and the *n*-alkylcyclopentane. The analysis of mass spectra [29] obtained for the saturated fraction allowed the identification of alkyl-methylcyclohexane having the same number of atoms of carbons on the two-dimensional plane (typical structures are reported in the insert in Fig. 5). A closer view to the alkanes also revealed that biomarkers (pristane and phytane) were fully resolved from alkanes. It is also worth noticing that these compounds eluted in the alignment of the band of the *n*-alkanes having the same number of atoms, i.e. 19 and 20.

In the case of the unsaturated fractions, especially in the case of LCO diesel, one should note the presence of aliphatic alkenes. In addition, the 1-alkenes could be evidenced by injection of standard compounds (typical structures are reported in the insert in Fig. 5). In the case of COK diesel sample, one should note the presence of compounds eluting just above the aliphatic alkenes and below aromatics. The elution of these compounds in the unsaturated fraction indicates that they corresponded to unsaturated compounds. Besides, their elution below the monoaromatic compounds clearly shows that these compounds did not contain any aromatic ring (in presence of an aromatic ring, such compounds would elute in the aromatic area). Owing to their retention upon the second dimension, it might be inferred that these compounds corresponded either to naphthenic alkenes or dialkenes. Indeed, the presence of a naphthenic ring or of an additional double bond would award more polarity than an alkyl chain but less polarity than an aromatic ring and these molecules would be more retained

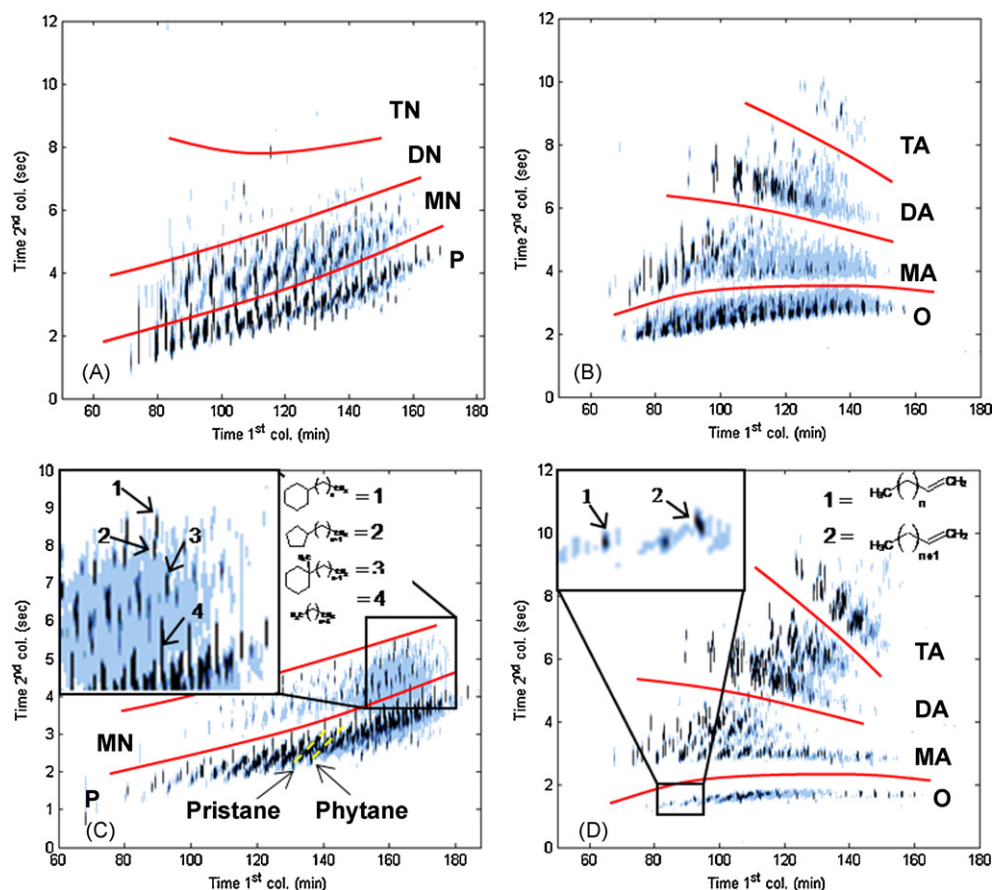


Fig. 5. Two-dimensional chromatograms of saturated and unsaturated fractions obtained by mean of SFC–twin-GC \times GC for LCO and COK diesels. operating conditions as in Sections 2.2 and 2.3. (A) Saturated fraction, diesel A; (B) unsaturated fraction, diesel A; (C) saturated fraction, diesel B; (D) unsaturated fraction, diesel B.

than aliphatic alkenes but less retained than monoaromatics on the second dimension. Even though no evidence regarding the exact nature of these molecules was found, it was finally assumed that these compounds corresponded to dialkenes that are known to occur in cokefaction samples such as considered diesel sample.

Thus, from a qualitative point of view, the identification of the main classes of hydrocarbons (i.e. alkanes, iso-alkanes, alkenes, naphthenes and aromatics) becomes possible, for the first time, in middle distillates.

3.4.2. Comparison of the SFC–twin-GC \times GC with reference methods

SFC–twin-GC \times GC separation described above was used to achieve the PIONA analysis of studied diesel samples (see Section 3.4.1 for experimental conditions). In order to monitor the performances of the system, model compounds (STD1) were injected regularly (after five analyses). Relative standard deviation over a 3-week period was found to be 0.044. For comparison purposes, group type analysis was also determined otherwise by mean of GC \times GC [31] and reference method ASTM D-2425 [32]. Quantitative results are reported in Table 4.

As can be seen from Table 4 and as could be expected from the powerful separation capacity of the SFC–GC \times GC system, significant discrepancies were observed between SFC–twin-GC \times GC and reference methods. For instance, olefinic derivatives could not be discriminated when GC \times GC or even MS was implemented while they were univocally identified when SFC–twin-GC \times GC was used. In the case of MS, alkenes and naphthenes break into the same ions and cannot be discriminated from each other, which resulted in their simultaneous quantitation. In the case of GC \times GC, the

Table 4

Recovery yields of test compounds contained in STD1. Experimental setup as in Section 2.2. Numbers refer to Figs. 4 and 5.

Compounds	Number	Recovery (%) Silver column
Tertiobutylcyclohexane	26	98
1-Decene	1	107
<i>n</i> -Decane	20	94
Indane	10	115
Indene	11	108
Transdecahydronaphthalene	27	101
Naphtalene	13	102
Tetraline	12	108
1-Dodecene	2	96
<i>n</i> -Dodecane	21	96
Ditertbutylbenzene	5	98
1-Methylnaphthalene	14	97
1,3,5-Triisopropylbenzene	6	97
1,3-Dimethylnaphthalene	15	104
1-Tetradecene	3	95
<i>n</i> -Tetradecane	22	97
1-Phenyldecane	7	113
1-Hexadecene	4	101
1-Phenyldecane	8	96
Octadecane	23	103
2-Methylanthracene	16	102
1-Phenyldecane	9	99
<i>n</i> -Eicosane	24	107
2-Ethylanthracene	17	109
2-Tertbutylanthracene	18	103
<i>n</i> -Docosane	25	105

Table 5
Comparison of SFC–twin-GC × GC with reference methods for group type analysis of middle distillates.

	Diesel A			Diesel B		
	SFC–twin-GC × GC	GC × GC	MS	SFC–twin-GC × GC	GC × GC	MS
Paraffins	14.87	15.24	11.1	21.45	17.91	21.7
Mononaphthenes	7.00	13.7	14.6	10.16	26.57	29.6
Dinaphthenes	0.00	0	–	3.72	11.7	–
Trinaphthenes	0.00	–	–	–	–	–
Monoaromatics	18.84	18.67	20.1	22.08	23.23	20.0
Diaromatics	30.58	33.28	43.75	14.9	16.35	24
Triaromatics	19.72	16.96	8.1	2.64	4.25	4.1
Tetraaromatics	0.99	1.1	2.3	0.99	0.0	0.2
Olefins	7.9	–	–	25.05 ^a	–	–
Sat/Aro	21.87/78.03	28.94/70.01	25.7/74.3	35.33/65.66	56.18/43.83	51.3/48.3

^a For convenience, diolefins contained in diesel sample B were quantitated as olefins.

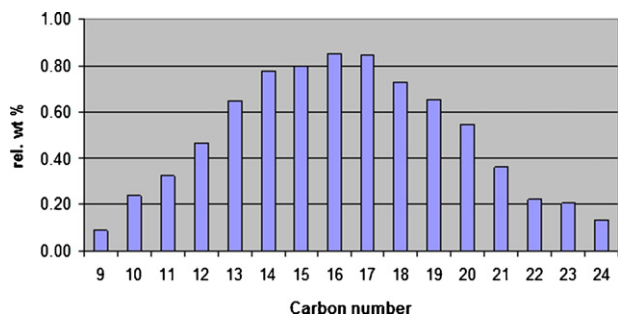


Fig. 6. Relative weight distribution of olefins in LCO diesel sample. Operating conditions as in Sections 2.2 and 2.3.

secondary column usually implemented did not provide enough selectivity to separate alkenes from naphthenes, leading to their quantitation. Therefore, these two reference methods systematically overestimated naphthenes at the expense of alkenes. For instance, considering diesel B, the bias between MS (respectively GC × GC) and SFC–twin-GC × GC roughly corresponded to 24% (respectively 23%) which also corresponded to the alkene content (25%)! Regarding the distribution of aromatics, good agreement was found between SFC–twin-GC × GC and GC × GC.

3.4.3. Determination of the alkene distribution by group of isomers

As mentioned previously, each class of hydrocarbons eluted in the form of bands of isomers on the two-dimensional chromatographic plane, which enabled the determination of their distribution by carbon number. As an illustration, the distribution of alkenes in diesel sample A was determined by external calibration; it is reported in Fig. 6.

Reported results demonstrate that the extended PIONA analysis (distribution by chemical class and by carbon number within each class) could be achieved in one single injection. These results are of major importance since the reactivity towards hydrotreatment certainly differs from one to another compound.

4. Conclusion

A new approach based on a three-dimensional chromatographic system has been proposed for PIONA analysis. For the first time, SFC has been hyphenated to twin comprehensive two-dimensional gas chromatography (twin-GC × GC) resulting in a highly resolutive analytical tool. SFC conditions as well as the SFC–GC × GC interface parameters have been extensively studied to achieve the complete separation of saturated and unsaturated compounds and their

quantitative transfer prior to their simultaneous analysis using a twin-GC × GC instrument.

The comparison of results with reference methods (GC × GC and MS) has also been proposed and clearly illustrates the benefits of SFC–twin-GC × GC approach (Table 5). The additional separation dimension prior to GC × GC allows unequalled quantification possibilities and reduces the risk of misidentification. For the first time, the extended PIONA analysis of middle distillates (i.e. the separation of hydrocarbons by chemical class and by carbon number) in one single injection could be reported.

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