

Comprehensive Two-Dimensional Gas Chromatography for Detailed Characterisation of Petroleum Products

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Résumé — Chromatographie en phase gazeuse bidimensionnelle pour l'analyse détaillée des produits pétroliers — La chromatographie gazeuse bidimensionnelle intégrale (CG×CG) représente une avancée majeure pour l'analyse détaillée des produits pétroliers. Cette technique est fondée sur deux dimensions orthogonales que forme l'association de deux colonnes de CG de sélectivités de séparation différentes. L'échantillonnage à haute fréquence à l'interface des deux colonnes permet que la totalité du produit soit transférée et analysée dans les deux dimensions. Ainsi, la capacité de pics et le pouvoir résolutif sont nettement accrus. En outre, les chromatogrammes 2D sont structurés en fonction des propriétés de volatilité et de polarité des hydrocarbures ce qui facilite leur identification. Dans cet article sont présentés les concepts et le principe de mise en œuvre de la CG×CG. Un système prototype a été développé à l'IFP comprenant notamment un modulateur à double-jets de CO₂ et un logiciel de post-traitement pour la visualisation et l'intégration des chromatogrammes. Les exemples d'application choisis illustrent le potentiel de la technique pour la caractérisation détaillée de distillats moyens, la spéciation de composés soufrés dans les gazoles et l'analyse approfondie des effluents de procédés pétrochimiques.

Abstract — Comprehensive Two-Dimensional Gas Chromatography for Detailed Characterisation of Petroleum Products — Comprehensive two-dimensional gas chromatography (GC×GC) is a major advance for the detailed characterisation of petroleum products. This technique is based on two orthogonal dimensions of separation achieved by two chromatographic capillary columns of different chemistries and selectivities. High-frequency sampling between the two columns is achieved by a modulator, ensuring that the whole sample is transferred and analysed continuously in both separations. Thus, the peak capacity and the resolving power dramatically increase. Besides, highly structured 2D chromatograms are obtained upon the volatility and the polarity of the solute to provide more accurate molecular identification of hydrocarbons. In this paper fundamental and practical considerations for implementation of GC×GC are reviewed. Selected applications obtained using a prototype of a GC×GC chromatograph developed in-house highlight the potential of the technique for molecular characterisation of middle distillates, sulphur speciation in diesel and analysis of effluents from petrochemical processes.

INTRODUCTION

The detailed characterisation of complex hydrocarbon samples is currently based on the separation, identification and quantification of the different constituents. It requires the highest resolution to be obtained in gas chromatography (GC) on a modern capillary column to provide high peak capacities. Owing to statistical peak overlap, the peak capacity of the separation system should be much higher than the actual number of components of a given mixture. Since the number of hydrocarbon isomers exponentially increases with the number of carbon atoms, GC becomes limited when dealing with samples containing more than 9 carbon atoms, and the detailed analysis of heavy naphtha or kerosene samples (*i.e.* C₈-C₁₅ as a carbon atom range) and middle distillate samples (C₁₅-C₃₀) is not possible.

Multidimensional chromatography (MDGC) was introduced in the 80s and 90s to overcome these limitations. According to the classical terminology in chromatography, separations are commonly called two - or multidimensional when separation of all or some selected groups of the sample's components are repeated in two or more analytical chromatographic columns of different selectivity (Giddings, 1995). Therefore, each dimension of separation is associated with a specific type of stationary phase and with a specific molecular interaction developed between this stationary phase and the solute. As stated by Giddings (1987), a multidimensional separation requires that:

- solutes are separated into two (or more) independent, or orthogonal, dimensions,
- the resolution achieved in one dimension is preserved during the whole separation.

Various multidimensional systems have been developed so far by hyphenating dimensions, whose nature can be different, such as liquid, gas or supercritical chromatography (Bertsch, 1999).

Better efficiency and easier implementation were achieved using two gas chromatography dimensions, which was obtained by coupling in series additional columns to the primary column in which the first separation is performed. In that case, the continuous transfer of the effluent or the transfer of selected fractions, or cuts, from the first to another column is achieved by the carrier gas flow which can be diverted to exit ("venting") or reversed for backflush by flow-rate switching between the columns. By the transfer of selected cuts from one column to another (different polarity and selectivity of the separation), the resolution between elution peak groups which are contained in such cuts is improved. This particular mode of operation in MDGC is called the heart-cutting technique (Di Sanzo *et al.*, 1988; Schomburg, 1995; Bertsch, 1999; Blomberg *et al.*, 2002). The increase in peak capacity of MDGC compared with conventional GC can usually be estimated by saying that the heart-cutting technique

provides $n_1 + n_2$ result, where n_1 and n_2 are the peak capacities of the first and the second columns, respectively. However, the information gained by the first separation (the chromatographic resolution) is partly lost when the cut is re-injected onto the second dimension, due to trapping or focusing processes (Mondello *et al.*, 2002).

Although genius separations can be performed using this so-called heart-cutting technique, drawbacks are related to the partial analysis of the sample in the two different dimensions and to the increased analysis time. Introduced in the early 1990s by Phillips and Liu (1991), comprehensive two-dimensional gas chromatography (GC×GC) was designed to overcome these limitations by producing a high-frequency heart-cutting separation of the entire sample. Ever since, GC×GC has evolved towards a strategic analytical tool sustained by improved instrumentation and has received considerable interest from the GC community, involving an increasing number of users working in a wide range of application areas (Bertsch, 1999; Ong and Marriott, 2002; Dallüge *et al.*, 2003; Blomberg *et al.*, 2002; Mondello *et al.*, 2002). The first two sessions of a dedicated symposium were held recently in Volendam (2003) and Atlanta (2004).

The principle, advantages and instrumentation of comprehensive GC×GC are detailed in the first part of this paper; the second part focuses on the development of a prototype in IFP labs and, finally, various applications are discussed in the third part to highlight the potential of GC×GC for investigating complex petroleum products.

1 PRINCIPLE AND IMPLEMENTATION OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

In the former MDGC system, only a limited part of the effluent of the first separation column will be directed towards the second one. In comprehensive GC×GC, the entire sample undergoes the two dimensions of separation without loss of resolution.

1.1 Principle

The principle of GC×GC (*Fig. 1*) is based on the hyphenation of two capillary GC columns of different selectivity connected through a modulation device, generally based on a cryogenic device (see 1.3). This interface enables sampling, focusing by trapping successive fractions of the effluent coming from the first column in narrow bands onto the second column and re-injection in a continuous way of sharp fractions of the first column's effluent into the second column. In that case, the entire sample is subjected to the two separation procedures and reaches the detector. Thus, this approach is truly comprehensive

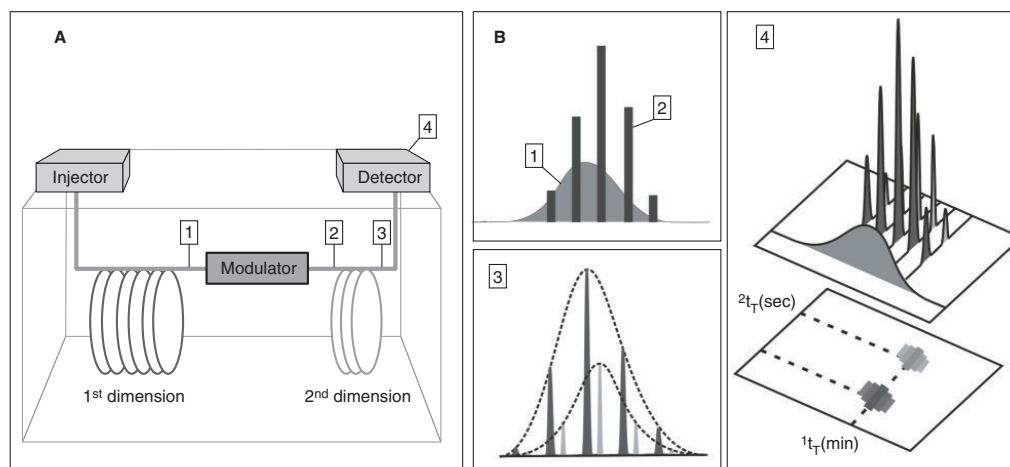


Figure 1

GCxGC instrumentation (A) and principle of modulation (B). See text for further explanation.

because, rather than a few selected fractions, the whole sample is separated on two different columns and no information gained during the first separation is lost during the second one.

Thus, two solutes co-eluting in the first separation may be separated in the second dimension provided that their interactions with the second stationary phase are different. Hence, a series of very fast separations in the second dimension is achieved simultaneously to the first-dimension separation. The raw modulated signal recorded by the detector is then processed for visualisation of 2D chromatograms where peaks are displayed as spots in a retention plane described as the first-dimension retention time in the x-axis and the second-dimension retention time in the y-axis. Intensity of peaks is indicated by colour gradation and this configuration can be viewed as the cartography of a sample. A 3D reconstruction may also be obtained, the third z -axis representing the peak intensity.

The modulation period (P_{mod}) is a key parameter for proper tuning of 2D separations, that should be chosen according to the duration of each second separation (${}^2t_{r,max}$) and to the width of peaks eluting from the first dimension (${}^1\omega$):

$${}^2t_{r,max} < P_{mod} < {}^1\omega / 3 \quad (1)$$

The first condition ensures that 2D chromatograms will be properly structured by avoiding wrapping around of analytes: this phenomenon occurs when highly retained peaks in the second dimension are eluted in the modulation cycle following that of their re-injection. The second condition is required to obtain a sufficient sampling of primary peaks and to avoid a loss of resolution in the first dimension.

The process can be summarised as shown in Figure 1; a peak eluting from the first column (1) is sampled by the modulator at a constant modulation period (P_{mod} , see below) (2). Each fraction is focused and re-injected into the second column for further separation (3). The signal recorded by the detector (4) is sliced according to the modulation period; the combination of secondary chromatograms and their projection in a retention plane allows the reconstruction of 2D chromatograms. The example also shows how overlapping peaks are effectively deconvoluted into two series of modulated peaks.

1.2 Advantages

The main advantages of GCxGC are here briefly discussed in terms of peak capacity, orthogonality and increased detectability.

1.2.1 Peak Capacity

The full peak capacity of GCxGC is assumed to be the product of individual peak capacities obtained in each dimension (Giddings, 1987; Giddings, 1995). For instance, if the first dimension has a peak capacity of 500 and the second one 5, the GCxGC system offers a peak capacity of 2500, which would require 10 million theoretical plates in a one-dimensional separation system, *i.e.* 50 times higher than the number available in GC.

1.2.2 Orthogonality

Orthogonality refers to the association of columns of different selectivities (Venkatramani *et al.*, 1996). Usually, a non-polar column is chosen for the first dimension and a

(semi-) polar column is used in the second dimension. This configuration leads to independent separation mechanisms for a temperature programme separation. The retention factor k of a compound in GC is related to its vapour pressure p_s and its activity coefficient in the stationary phase at infinite dilution γ^∞ according to the following equation:

$$k \propto \frac{1}{p_s \tilde{a}} \quad (2)$$

In the first dimension, activity coefficients are close to unity owing to the lack of specific interactions; the retention only depends on the vapour pressure and solutes are separated according to their boiling point order, using a gradient of temperature. The second dimension can be considered as isothermal since it takes only a few seconds and the ramp of the temperature achieved for the first-dimension separation is relatively low (typically, 1 to 2°C/min). Thus, for one modulation cycle, the second separation is performed at constant temperature corresponding to the temperature at which solutes are re-injected into the second column; owing to the temperature gradient, it increases from cycle to cycle. In these conditions, volatility effects are non-discriminative in the second dimension and only specific interactions govern the retention. A reverse-type configuration (first polar and second non-polar columns) was also shown to be orthogonal (Vendeuvre *et al.*, 2005a).

Orthogonality in GC×GC leads to structured chromatograms, which can be represented as a two-dimensional plane from which elution peaks emerge:

- the first dimension of this plane represents the retention time on the first column, which is usually expressed in minutes;
- the second dimension represents the retention time on the second column, which is usually expressed in seconds;
- the third dimension represents the signal intensity, although the usual way to represent a GC×GC chromatogram is a two-dimensional contour plot.

As an example, the different chemical groups of petroleum products (saturates, mono-, di- and triaromatics) are then localised in specific areas of the chromatogram, which facilitates identification. The typical bands observed for isomer groups, known as the roof-tile effects, also contribute to confirming peak assignment (Schoenmakers *et al.*, 2000).

1.2.3 Detectability

Finally, mass conservation and peak compression in the modulator involve a signal increase of approximately 50 times the peak height. Indeed, the advantage of solute focusing by trapping and desorption with high heating and cooling time constants relies on the possibility of reversing the peak dispersion occurring in any chromatographic

process (De Gueus, 1998). The modulation of the primary peak results in a series of sharp peaks with a peak width below 100 ms. Owing to mass conservation, the narrow peaks have a high amplitude. The signal intensity enhancement is typically ten- to seventyfold higher in GC×GC than in GC. However, regarding the analyte detectability, the signal to noise (S/N) ratio has to be evaluated. As GC×GC requires high acquisition frequency of detectors (minimum 100 Hz) to properly define very narrow peaks, the noise increases according to the square root of acquisition frequency and the expected signal intensity enhancement is reduced. However, a gain in sensitivity by a factor of 5 is generally achieved (Lee *et al.*, 2001). Hence, the focusing effect of modulation is a decisive advantage when analysing traces or low-concentrated compounds in complex matrices (Bertoncini *et al.*, 2005).

1.3 Modulation Technology

A variety of modulators, either valve-based or thermal systems, have been developed so far to ensure complete and on-line transfer of the sample between the two columns of GC×GC, with a focusing effect generating sharp peaks with widths at half-heights as low as 100–300 ms.

Figure 2 shows the different modulators and the modulation process inside the modulator.

For valve-based modulators, sampling of the effluent is achieved via valve-switching at a high frequency; focusing is obtained using a secondary circuitry of higher flow-rate carrier gas. These systems are rather limited and complicated even though drawbacks related to incomplete sampling and inherent temperature restrictions have recently been resolved with the introduction of a differential flow modulator (Bueno and Seeley, 2004).

- Thermal modulation, either heating or cryogenic, is based on a succession of trapping / desorption cycles obtained by positive or negative temperature differences applied at the two columns' "interface". For heated modulators trapping is achieved in a tube with a thick film of stationary phase and desorption occurs by applying locally a higher temperature of about 100°C compared with the oven temperature. The first system designed by Liu and Philips consisted of a resistively heated modulator: solutes were trapped in the modulation tube coated with a metallic painting and desorption was achieved by generating periodic hot pulses from current pulses (Liu and Phillips, 1991). Because of lack of robustness, this system was replaced by a rotating heated assembly (sweeper) moving around the modulator tube, the speed of revolution defining the modulation period (Phillips *et al.*, 1999). The main drawback of a heated modulator is the temperature limit, preventing the analysis of compounds heavier than C₂₅.

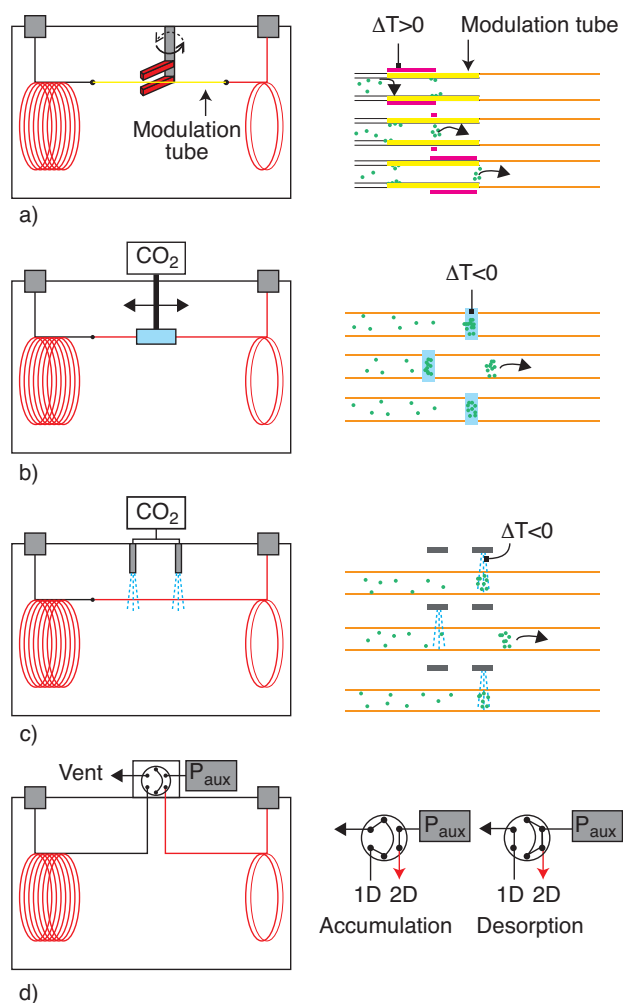


Figure 2

The different modulation systems and their process of modulation. From top to bottom : Sweeper modulator - Longitudinally Modulation system - Dual-jets CO₂ modulator - Valve-based modulator.

- For cryogenic modulators, trapping is achieved by the decrease in temperature (about -100°C) generated by the endothermic expansion of a cryogen such as carbon dioxide or liquid nitrogen; desorption occurs when solutes are exposed again to an oven temperature. For cryogenic modulator trapping, there is no need for a particular tube between the two columns. The LMCS (Longitudinally Modulation Cryogenic System) generates modulation by moving back and forth a cryogenic CO₂ spray along the head of the second column (Marriott and Kinghorn, 1997; Kinghorn and Marriott, 2000). The dual-jets CO₂ modulator enables modulation by turning on and off two sprays of CO₂ applied on the column (Beens *et al.*, 2001). The cryogenic approach is devoted to a wider boiling point range of volatile compounds but liquid nitrogen should be preferred to CO₂ for

trapping of very volatile solutes. The static strategy of jet modulation is obviously more robust and of easier implementation than the mobile one (sweeper and LMCS). Two commercial systems using the jet technology supplied by Thermo and Leco under Zoex licensing are now available.

1.4 Chromatographic Column Features

Since the GC×GC system relies upon fast analysis of accumulated bands, it is usual to perform the first dimension to obtain a conventional GC elution and the second dimension in fast GC conditions (Beens *et al.*, 2000). The features of the first dimension are not crucial versus those of the second column: the second dimension must enable the achievement of the complete separation of pulsed bands within the modulation period of the system. This is most effectively achieved by using a short, narrow-bore thin-film column. A typical column set might comprise a $25\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ column in the first dimension followed by a $1\text{ m} \times 0.1\text{ mm} \times 0.1\text{ }\mu\text{m}$ column as the second dimension.

Considering the nature of the stationary phases, it is necessary to use analytical columns that provide independent separation mechanisms in the first and the second dimensions in order to create orthogonal separation conditions. Every separation in GC is based on volatility and on interactions depending on the chemistry of the stationary phase, *i.e.* dispersive, hydrogen bonding, π - π , etc. Therefore, in order to achieve true orthogonality, the first dimension should be non-polar, such as a 100% dimethylpolysiloxane phase (Phillips and Xu, 1995), and the second one more polar to enable specific interactions.

2 DEVELOPMENT OF AN INNOVATIVE GC×GC PROTOTYPE

2.1 GC×GC Hardware

IFP launched a research programme in 2002 to evaluate GC×GC as a breakthrough technique for the molecular characterisation of petroleum products. Owing to the limited performances of available commercial apparatus as well as the lack of efficient software at that time, a prototype was developed in-house. A dual-jets CO₂ modulator was built according to the description given by Beens *et al.* (2001). A programmable automation controller (provided from Opto22) generates very precisely two sequences of out-of-phase voltage pulses synchronised with the chromatograph start time. This allows the opening and the closing of two electrically-driven valves (Asco) mounted on the upper wall of the gas chromatograph. Liquid CO₂ (industrial quality) is then forced into a restricted section tubing to form a cold spray directed on the column. Temperature measurements showed a decrease in 100°C in the jet, whereas the surrounding air in the GC oven was not significantly disturbed.

2.2 GC×GC Software

A dedicated program was developed under MatLab 6.5 for data processing in GC×GC (*Polychrom*). It is based on the conversion of raw data (time - intensity) into a matrix format where the number of lines equals the modulation period multiplied by the acquisition frequency, the number of columns represents the number of modulation cycles and the matrix elements are the values of signal intensity. Different operations are available for the visualisation and quantification of GC×GC data. Chromatograms may be displayed in one, two or three dimensions and visualisation functions include second-dimension offsets, intensity threshold, smoothing, filtering and background subtraction. Quantification in GC×GC-FID is achieved as in GC-FID by considering that the signal response (peak area) is proportional to concentration. As the modulation process slices the quantity of one component into several fractions, it is necessary to sum up all the modulated peak areas corresponding to this compound (Dallüge *et al.*, 2003). Integration of chromatograms consists of selecting a blob (containing one or several peaks) by drawing a polyedric contour around it using mouse clicking and calculating its area and its retention times. This process was shown to be reliable, since the discrepancies of quantification results obtained from the separation of a synthetic mixture of hydrocarbons using GC×GC and GC were lower than 3%. The start and stop times of secondary peaks calculated by the integration software of the chromatograph can be visualised and superposed on the 2D chromatogram: this specific function facilitates manual drawing of blob contours, in particular for determining peak valleys for partially resolved secondary peaks. Besides, a dedicated function was introduced for the calculation of simulated distillation (SD) curves for one selected blob, and it may be advantageous to determine group-type SD profiles.

3 APPLICATIONS

Selected applications of GC×GC to various analytical challenges encountered in the petroleum industry for which conventional techniques show limitations are presented: molecular characterisation and sulphur speciation of middle distillate samples and detailed analysis of petrochemical effluents.

3.1 Enhanced Molecular Characterisation of Diesel Fuel Samples

Conventional techniques used for the characterisation of diesel fuels are directed towards either the determination of group-type classification or the boiling point range distribution.

The former is usually performed by liquid chromatography (LC) for the saturate/aromatic balance (ASTM D2549)

or by mass spectrometry (MS) providing the repartition of hydrocarbons in up to 11 families (ASTM D2425).

The latter is obtained by GC simulated distillation (ASTM D2887). The aim of our work was to show that GC×GC simultaneously provides both types of information with a better insight into the petroleum cut (Vendevre *et al.*, 2005).

Figure 3 A, C and D represents GC×GC chromatograms of a straight-run sample obtained by the distillation of Safaniya oil (boiling point range from 213 to 347°C) in 1D, 2D and 3D views, respectively. The experimental set-up is given in Table 1.

TABLE 1
Operating conditions for GC×GC separation of diesel fuels

Columns	PONA ^a , 10 m × 0.2 mm i.d.; 0.5 µm BPX50 ^b , 0.8 m × 0.1 mm i.d.; 0.1 µm
Column oven	50-280°C; 2°C/min
Carrier gas	He; constant pressure, 200 kPa
Injection	0.2 µL, split ratio 1:100, 280°C
Detector	FID, 300°C
Acquisition rate	100 Hz
Modulation period	7 s

^adimethylpolysiloxane, Agilent Technologies (Massy, France).

^b(50%phenyl)polysilphenylene-siloxane, SGE (Courtabœuf, France).

As can be seen from the raw chromatogram (1D), an impressive number of peaks can be observed (more than 30 000 individual peaks have been integrated from raw data), preventing a simple interpretation of the chromatogram. However, Figure 3B shows the second-dimension separation, obtained for one modulation cycle, of about ten peaks eluted from the polar column (BPX50) according to the number of aromatic rings, as the BPX50 stationary phase contains a significant amount of phenyl groups that preferentially interact with aromatic compounds through π - π interactions. Thus, on this column, saturates elute first then monoaromatics, diaromatics and triaromatics, while all these compounds are potentially co-eluted in the first dimension. This is a demonstration of the higher resolving power of GC×GC.

After data processing, the structure of the 2D chromatogram is evidenced (*Fig. 3C*). This group-breaking technique offers a polarity versus volatility separation of the sample, leading to a two-dimensional chromatogram:

- In the first dimension, hydrocarbons are eluted according to their increasing boiling point, or number of carbon atoms.
- The selectivity of the second dimension allows the separation of hydrocarbons from the least to the most

polar, mainly according to the number of aromatic rings in that case.

Group-type bands are then easily distinguished and the contour of each group is adjusted using a specific function of the program indicating peak valleys, the density of which being more abundant at the border between two groups.

Finally, the 3D chromatogram (Fig. 3D) conveniently indicates the relative concentrations of hydrocarbons, but this representation is not suitable for quantitative purposes.

Integration of group-type bands, *i.e.* saturates, mono-, di- and triaromatic hydrocarbons determined in the GC×GC chromatograms, was achieved using the software. Comparison with results obtained by liquid chromatography and mass spectrometry (Table 2) demonstrates that the results are in line with ASTM methods, and the validity of GC×GC (Vendevre *et al.*, 2005).

TABLE 2

Composition (% w/w) of the diesel obtained by LC, MS and GC×GC

	LC (n=4)	MS (n=10)	nP-GC×GC (n=3)
saturates	70.4 ± 0.3	71.7 ± 0.9	70.6 ± 0.6
monoaromatics		18.8 ± 0.4	18.0 ± 0.3
diaromatics		8.7 ± 0.2	10.3 ± 0.3
triaromatics		0.8 ± 0.1	1.1 ± 0.1

Contrary to standard methods, a more detailed characterisation of diesel can be obtained from the structure of GC×GC chromatograms. Indeed, isomers are grouped in the same location of the chromatogram and can be recognised owing to the roof-tile effect. Clearly, the resolution is still insufficient to allow individual peak identification except for the first (un-alkylated) members of a chemical family (naphthalene, anthracene and phenanthrene).

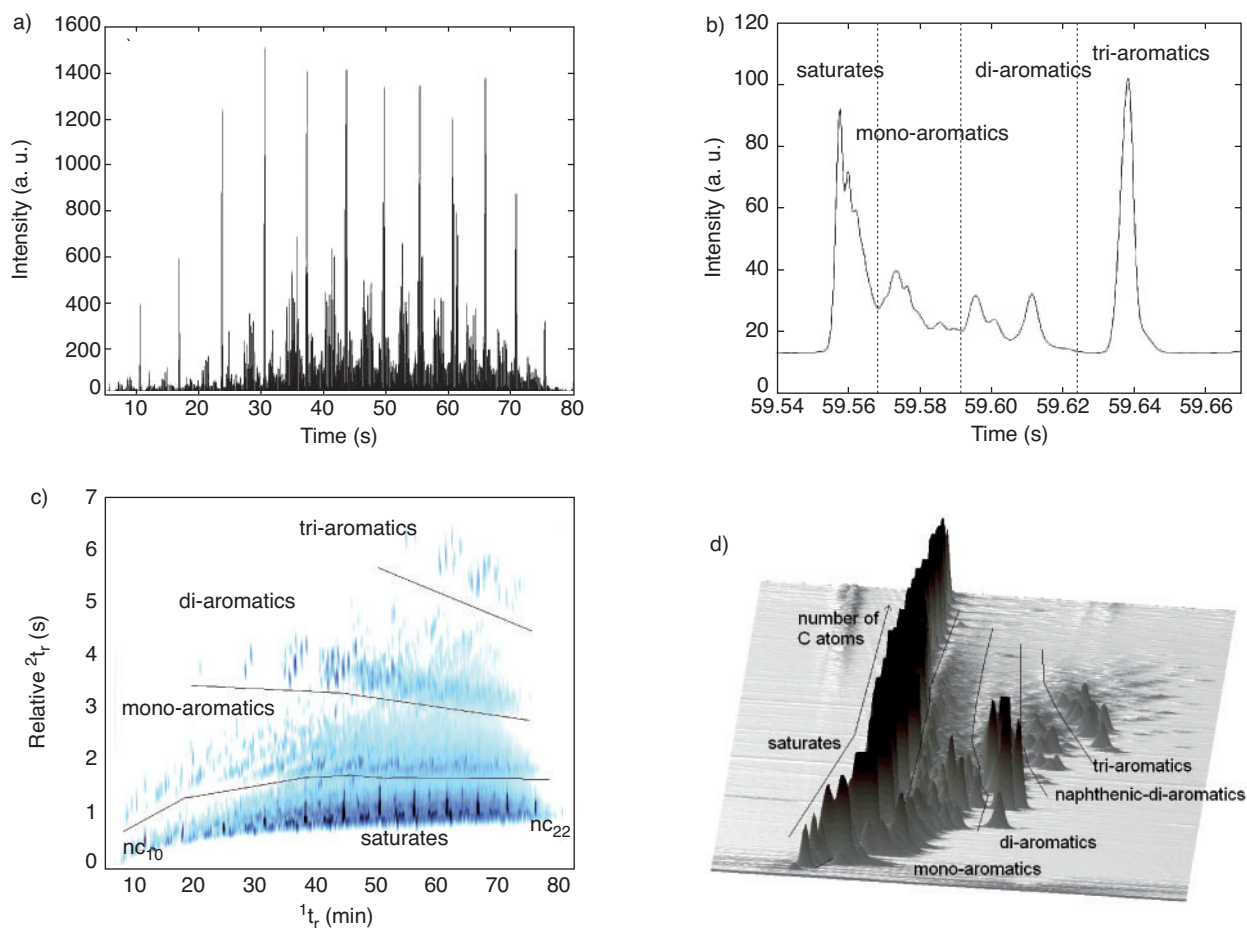


Figure 3

Chromatograms of a straight-run diesel sample obtained in one dimension - raw data- (a), two dimensions (c) and three dimensions (d). An enhanced view of raw data during a modulation period is shown (b).

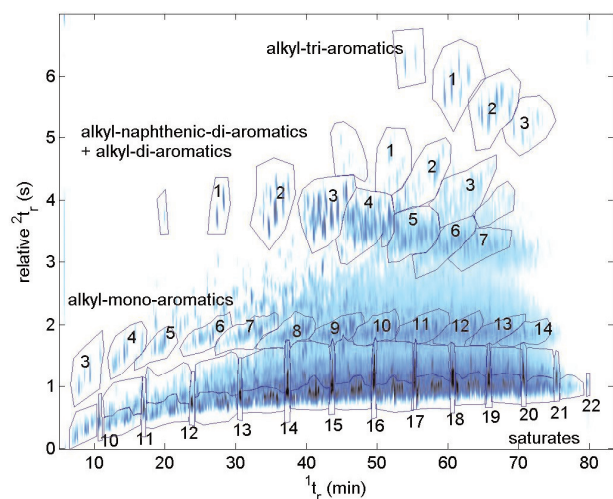


Figure 4

Clusterisation of a 2D chromatogram. The number inside each cluster indicates the number of carbon atoms of the alkyl group or alkyl chain.

However, isomers are grouped in the same location of the chromatogram, and can be recognised owing to the roof-tile effect. The tricky definition of elution zones was partly confirmed by injection of standards (*Fig. 4*).

Once integration is completed, this rather new kind of determination offers the possibility of assigning to each cluster of isomers a macroscopic property, such as mass, viscosity or cetane number, which can be known for each isomer group, resulting in more accurate information on physico-chemical properties of the diesel cut. In one single analysis, the complete characterisation of the sample could be obtained and then directly compared with product speci-

cations; more precise and reliable kinetic and thermodynamics models that can be applied to the operation of hydrodesulphurisation (HDS) units are also expected. There is no doubt that the 2D-GC, which is able to provide the composition of a petroleum sample in paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) separation, will rapidly become the industrial benchmark.

However, the clusterisation of a petroleum cut has limitations related to the partial overlapping, in the first dimension, of two adjacent series of aromatic isomers resulting from the higher volatility of highly alkylated aromatics than linear alkyl aromatics having one carbon atom less. Instead of performing the discrete characterisation as described above, continuous information can be extracted from GC×GC chromatograms by using Simulated Distillation (SimDis) curves that can be obtained in a similar manner to GC-SimDis. The decisive advantage of GC×GC relies on the possibility of drawing a specific SimDis curve for each chemical group. Once a group-type band is selected, it is sliced according to the modulation period. The program automatically generates a report that allows the construction of SimDis curves from the boiling point and the cumulated weight percent: the first-dimension retention time of each slice is converted into a boiling point using a relationship established with n-paraffins; the area of each slice determines a weight percent using specific response factors. Figure 5 shows the SimDis curves obtained for saturates, mono-, di-, and triaromatics, as identified in Figures 3-4. The global SimDis curve obtained by summing group-type SimDis curves fits perfectly with the ASTM D2887 SimDis curve, the discrepancies being lower than 1°C over the range 10-90% and lower than 2.5°C over the range 5-95%.

Characterisation tools developed from GC×GC were applied to studying the effectiveness of a conversion

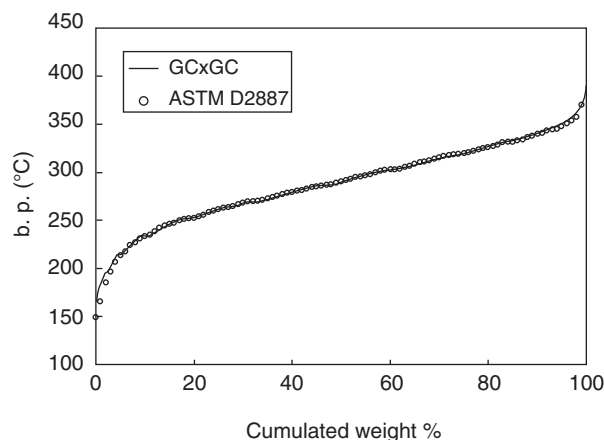
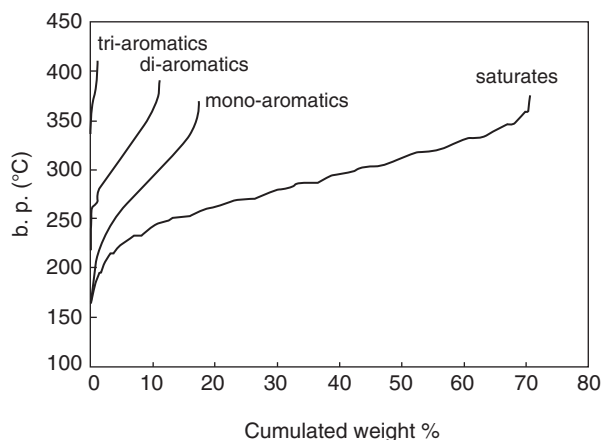


Figure 5

Group-type Simulated Distillation curves for a straight-run diesel sample.

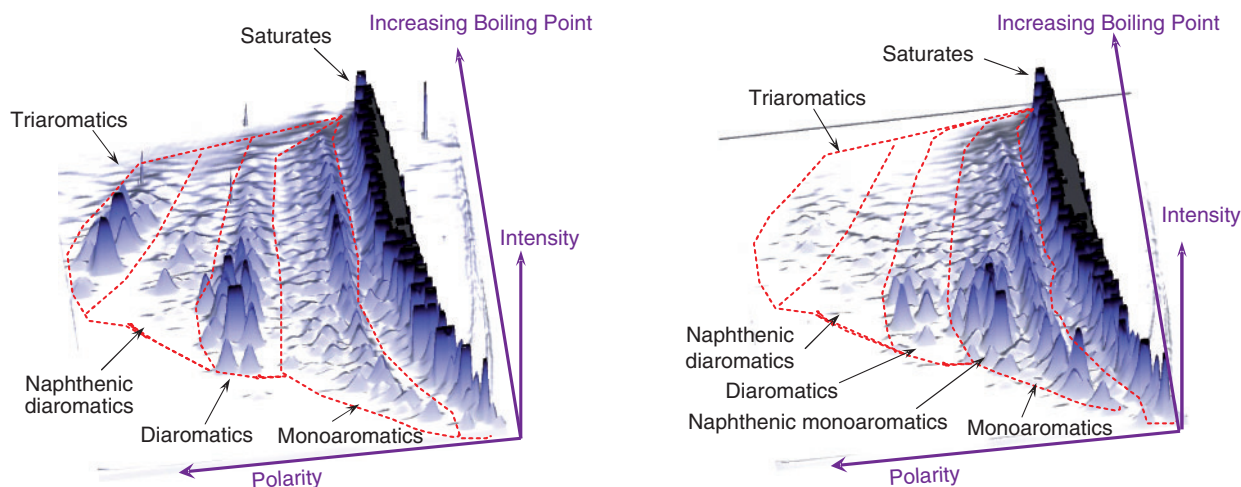


Figure 6

3D chromatograms of the feed and the product from the hydrotreatment process of a straight-run diesel sample.

process. GC×GC chromatograms of the feed and the product of a hydrotreatment process are shown in Figure 6. Qualitative comparison of 3D chromatograms highlights the transformation of triaromatic and diaromatic compounds into naphtho-monoaromatic compounds of lower polarity (lower retention in the second dimension). The conversion of polyaromatics into naphtho-monoaromatics during the hydrodearomatisation (HDA) process can be followed at the molecular level and the activity of the catalyst for HDA can be understood and quantified better. The results obtained are used to optimise kinetics models and process operations.

In addition, GC×GC SimDis curves of the feed and the product were plotted for saturate, mono-, di- and triaromatic hydrocarbons (Fig. 7). The shift of SimDis curves demonstrates partial removal of di- and triaromatics to form monoaromatics and saturates, mainly consisting of naphthenic species. Thus, GC×GC is a powerful tool to evaluate qualitatively and quantitatively the performances of a conversion process, as slight modifications in composition can be evidenced by differences in the retention map and by the shift of group-type SimDis curves.

3.2 Sulphur Speciation

More stringent specifications on sulphur content in gasoline and diesel as well as production of non-conventional oil with high sulphur content have strengthened the need for deeper desulphurisation (hydro-desulphurisation, HDS) of petroleum feedstocks. Thus, sulphur speciation, which consists of the determination of the repartition of different chemical classes of sulphur compounds (sulphides, thiophenes, benzothiophenes

and dibenzothiophenes) according to the number of carbon atoms, is of major interest for refiners, in order to improve kinetics modelling based on molecular composition. Usually, sulphur speciation is achieved using the hyphenation of gas chromatography to Sulphur Chemiluminescence Detection (GC-SCD) or using mass spectrometry, but these techniques become rather limited when complex samples are analysed. GC×GC was hyphenated to SCD to increase the resolution of the chromatographic separation (Ruiz-Guerrero *et al.*, 2006).

GC-SCD and GC×GC-SCD chromatograms are compared in Figure 8 for two different straight-run samples,

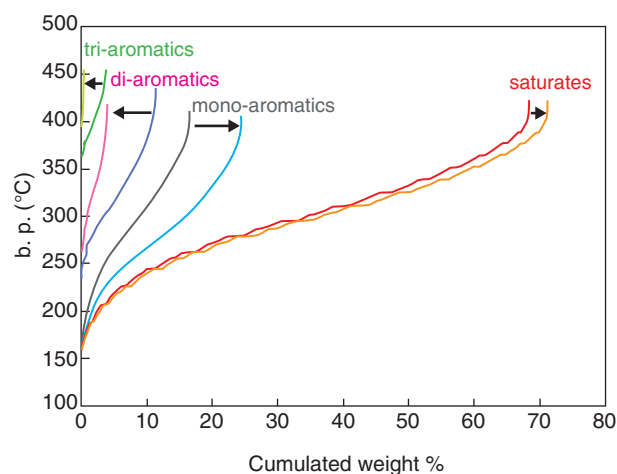


Figure 7

Group-type Simulated Distillation curves for the feed and the product of hydrotreatment of a straight-run diesel sample.

TABLE 3
Operating conditions for GC×GC-SCD and GC-SCD analyses

	GC×GC-SCD	GC -SCD
Column(s)	PONA ^a , 10 m × 0.2 mm i.d.; 0.5 µm BPX50 ^b , 0.8 m × 0.1 mm i.d.; 0.1 µm	DB1 ^c 60 m × 0.25 mm i.d.; 0.25 µm
Column oven	50–280°C; 2°C/min	65–120°C; 10°C/min 120–240°C; 1°C/min 240–280°C (10min); 10°C/min
Carrier gas	He; constant pressure, 200 kPa	He; constant flow, 2 mL/min
Injection	1 µL, split ratio 1:50; 280°C	0.5 µL, split ratio 1:50; 270°C
Detector	SCD, 800°C	SCD, 800°C
Acquisition rate	50 Hz	5 Hz
Modulation period	8 s	-

^a dimethylpolysiloxane, Agilent Technologies (Massy, France).

^b (50%phenyl)polysilphenylene-siloxane, SGE (Courtabœuf, France).

^c J&W Scientific.

obtained from the distillation of Middle-Eastern (SR1) and South-American (SR2) crude oil. Experimental conditions are reported in Table 3. GC-SCD chromatograms show a significant baseline drift due to the co-elution of several sulphur compounds. Besides, it is generally assumed that all alkyl-BT are eluted before DBT, whereas partial co-elution is evident when looking at the GC×GC chromatograms. Owing to the selectivity of the second dimension, GC×GC-SCD allows the separation of alkyl-BT from alkyl-DBT, the latter being more retained on the polar column due to the presence of an additional aromatic ring. Hence, two well-resolved bands of alkyl-BT and alkyl-DBT are obtained for the SR1 sample, and a carbon atom breakdown inside each band allows the quantification of alkyl-BT until C₉ and of alkyl-DBT until C₅ (Table 4). A similar distribution is obtained for the SR2 sample, except for the relative concentration of a third group constituting sulphides and thiophenes, which can also be identified and separated from alkyl-BT and alkyl-DBT owing to the lower polarity of these compounds. This third group is not taken into account in GC-SCD analysis, whereas it represents 60% of the sample of SR2. For the sample SR1, only traces of these compounds were quantified (< 8%) and are not represented in Figure 8 due to the level of the baseline. Thus, GC×GC allows the discrimination of straight-run samples from different origins and provides the quantitative repartition of alkyl-BT and alkyl-DBT groups according to the number of carbon atoms. No other analytical technique currently reaches this level of resolution.

This added knowledge is of significant value in the determination of the operating conditions required to attain product specifications with given feedstocks, and can be used to advantage for optimisation of the HDS process in plant operations (space velocity, H₂ partial pressure and reaction temperature).

TABLE 4
Detailed group-type distribution using GC-SCD and GC×GC-SCD for SR1 and SR2

	SR1			SR2		
	GC	GC×GC	RSD	GC	GC×GC	RSD
Alkyl-thiophenes + sulfides	-	8.3	0.5	6.6	50.9	0.9
BT	-	0.1	0.0	0.3	0.0	0.0
C1-BT	0.2	0.8	0.0	3.2	0.6	0.0
C2-BT	2.0	1.9	0.1	5.7	2.5	0.0
C3-BT	4.6	2.9	0.4	5.4	5.1	0.3
C4-BT	8.5	4.6	1.1	6.1	8.5	0.2
C5-BT	-	7.4	0.4	-	7.6	0.2
C6-BT	-	9.2	0.5	-	5.2	0.2
C7-BT	-	6.1	0.1	-	5.3	0.5
C8-BT	-	7.9	0.2	-	4.6	0.1
C9-BT	-	4.4	0.4	-	3.5	0.3
DBT	1.4	0.8	0.0	0.5	0.1	0.0
C1-DBT	8.9	4.6	0.0	2.9	0.6	0.0
C2-DBT	8.9	7.4	0.1	1.2	0.9	0.1
C3-DBT	11.9	7.9	0.4	2.6	1.6	0.2
C4-DBT	-	8.3	0.0	-	2.9	0.4
C5-DBT	-	4.8	0.1	-	-	-
Others	53.5	12.6	0.7	65.7	0.0	0.0

RSD are the relative standard deviations in GC×GC.

- Not present.

3.3 Dehydrogenation of n-paraffins / Linear Alkyl-Benzene Synthesis

Linear alkyl-benzenes are highly valuable products in petrochemistry, especially for their use as surfactants. They can be obtained from the addition of linear olefins on aro-

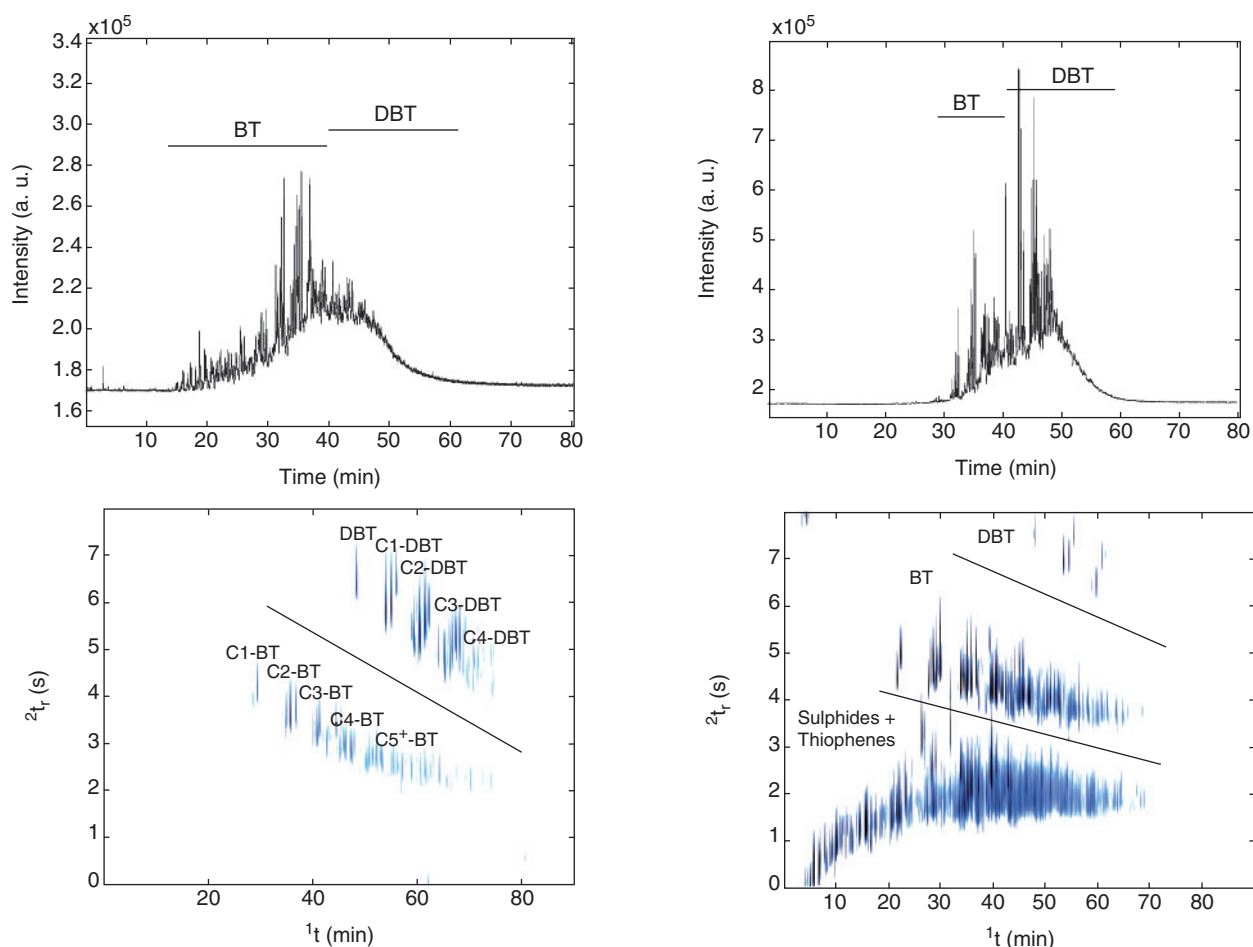


Figure 8
GC-SCD and GCxGC-SCD chromatograms of SR1 and SR2 straight-run samples.

TABLE 5
Operating conditions for GCxGC separation of petrochemical samples

	Dehydrogenation of n-paraffins	LAB synthesis
Columns	PONA ^a , 20 m × 0.2 mm i.d.; 0.5 μm BPX50 ^b , 1.1 m × 0.1 mm i.d.; 0.1 μm	PONA ^a , 10 m × 0.2 mm i.d.; 0.5 μm BPX50 ^b , 1.6 m × 0.1 mm i.d.; 0.1 μm
Column oven	50–280°C; 2°C/min	50–280°C; 2°C/min
Carrier gas	He; constant pressure, 250 kPa	He; constant pressure, 200 kPa
Injection	0.5 μL, split ratio 1:100, 280°C	0.5 μL, split ratio 1:100, 280°C
Detector	FID, 300°C	FID, 300°C
Acquisition rate	100 Hz	100 Hz
Modulation period	4 s	6 s

^a dimethylpolysiloxane, Agilent Technologies (Massy, France).

^b (50%phenyl)polysilphenylene-siloxane, SGE (Courtabœuf, France).

matic rings, and linear olefins are produced by the reaction of dehydrogenation of n-paraffins. Both reactions lead to the formation of secondary products, which are often undesirable. Hence, it is crucial to precisely determine the nature and the content of these species in order to evaluate

the best operating conditions of the units that avoid their formation. Owing to the limitations encountered with GC, GCxGC was investigated for detailed characterisation of effluents from these two reactions (Vendevre *et al.*, 2004). Experimental conditions are reported in Table 5.

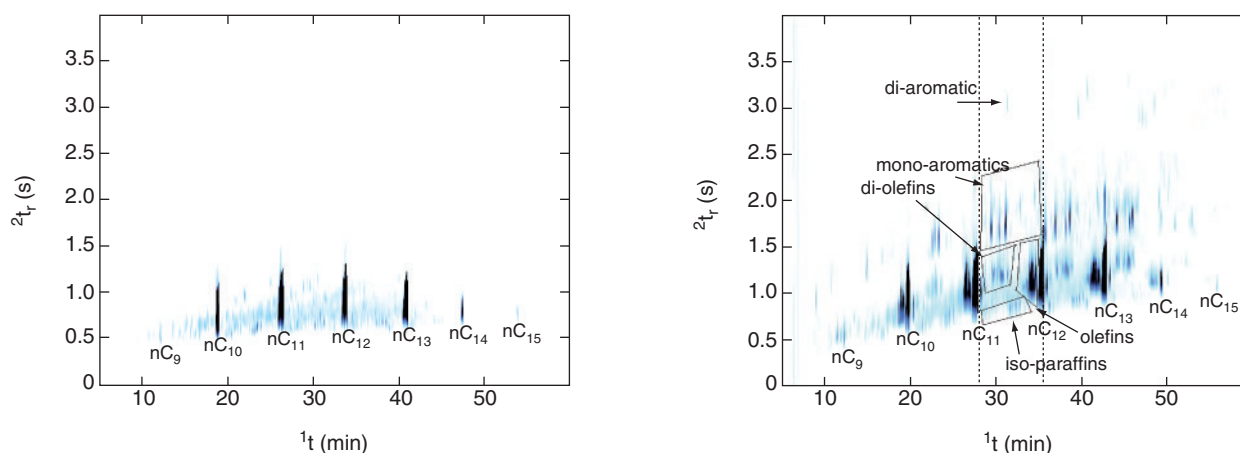


Figure 9

GCxGC chromatograms of the feed and the product from the reaction of dehydrogenation of n-paraffins.

The feed and the product converted at 20% in the reaction of dehydrogenation of n-paraffins were analysed using GCxGC (Fig. 9). The structure of the chromatograms allows for the identification of the nature of the compounds formed during the reaction. The feed mainly contains n-paraffins and no aromatics. The selectivity of the second dimension allows the monitoring of products formed after reaction. Olefins are major products of reaction while diolefins, aromatics and diaromatics are also produced at low levels. The formation of these secondary species should be avoided because they are responsible for the catalyst coking or polymerisation. The advantage of GCxGC relies on the possibility of precisely monitoring the forma-

tion of reaction products whose polarity is different from that of the matrix.

The GCxGC chromatogram of the product of synthesis of linear alkylbenzenes (LAB) is shown in Figure 10. This product is principally a mixture of decyl-, dodecyl- and tetradecyl-benzenes. A roof-tile effect results from the arrangement of isomers in the retention plane. Branched-chain isomers are also present (dialkyl benzene, DAB). Contrary to a conventional GC analysis, alkyl-benzenes substituted by a naphthenic group were also evidenced owing to their slightly higher polarity and the resulting greater retention times in the second dimension. This resolution was achieved using a longer second column to increase the selectivity in that dimension.

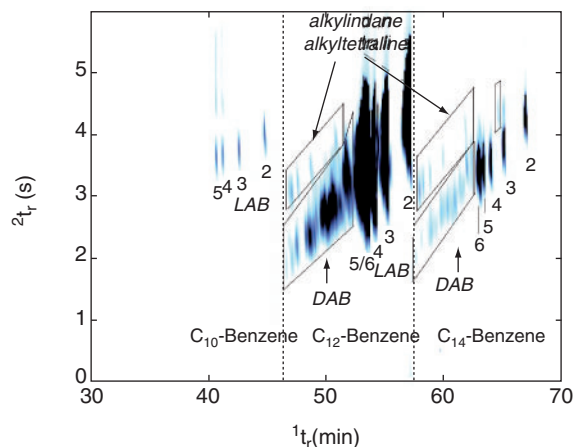


Figure 10

GCxGC chromatograms of the product from linear alkylbenzene (LAB) synthesis. The number refers to the position of the benzyl group on the main alkyl chain.

CONCLUSION

Comprehensive two-dimensional gas chromatography demonstrates unequalled performances for the detailed characterisation of complex hydrocarbon samples. Two-dimensional chromatograms provide higher peak capacities compared with GC and the combination of a volatility-based and a polarity (aromaticity)-based separation allows easier and more reliable identification of hydrocarbons. The development of a prototype at IFP including modulation technology and data-processing software allowed the achievement of high-resolutive and ordered separations of middle distillates. An original way of generating GCxGC SimDis curves for all different chemical groups has been presented and applied to highlight the effect of a hydrotreatment process on chemical composition. GCxGC can be hyphenated to all GC detectors that possess high-frequency acquisition. In this study the GCxGC-SCD was

implemented to obtain speciation of sulphur compounds in middle distillates. Future work will concern hyphenation with time-of-flight mass spectrometry.

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REFERENCES

- Beens, J., Blomberg, J., Schoenmakers, P.J. (2000) Proper tuning of comprehensive two-dimensional gas chromatography to optimize the separation of complex oil fractions. *J. High Res. Chromatog.*, **23**, 182-188.
- Beens, J., Adahchour, M., Vreuls, R.J.J., van Altena, K., Brinkman, U.A.Th. (2001) Non-moving Modulation Interface for Comprehensive Two-Dimensional Gas Chromatography. *J. Chromatogr. A*, **919**, 127-132.
- Bertoncini, F., Vendeuvre, C., Thiébaud, D. (2005) Interest and Applications of Multidimensional Gas Chromatography for Trace Analysis in the Petroleum Industry. *Oil Gas Sci. Technol.*, **60**, 937-950.
- Bertsch, W. (1999) Two-dimensional gas chromatography. Concepts, instrumentation, and applications. *J. High Res. Chromatog.*, **22**, 647-655.
- Blomberg, J., Schoenmakers, P.J., Brinkman, U.A.Th. (2002) Gas chromatographic methods for oil analysis. *J. Chromatogr. A*, **972**, 137-173.
- Bueno, P.A., Seeley, J.V. (2004) Flow-switching device for comprehensive two-dimensional gas chromatography. *J. Chromatogr. A*, **1027**, 3-10.
- Dallüge, J., Beens, J., Brinkman, U.A.Th. (2003) Comprehensive two-dimensional gas chromatography : a powerful and versatile analytical tool. *J. Chromatogr. A*, **1000**, 69-108.
- De Geus, H.-J., De Boer, J., Brinkman, U.A.Th., Ledford Jr., E.B., Phillips, J.B. (1998) Increased signal amplitude due to mass conservation in a thermal desorption modulator. *J. High Res. Chromatog.*, **21**, 411-413.
- Di Sanzo, F.P., Lane, J.L., Yoder, R.E. (1988) Application of the state-of-the-art multidimensional high resolution gas chromatography for individual component analysis. *J. Chromatogr. Sci.*, **26**, 206-209.
- Giddings, J.C. (1987) Concepts and comparisons in multidimensional separation. *J. High. Res. Chromatog.*, **10**, 319-323.
- Giddings, J.C. (1995) Sample dimensionality: a predictor of order-disorder in component peak distribution in multidimensional separation. *J. Chromatogr. A*, **703**, 3-15.
- Kinghorn, R.M., Marriott, P.J. (2000) Enhancement of Signal-to-Noise Ratios in Capillary Gas Chromatography by Using a Longitudinally Modulated Cryogenic System. *J. High Res. Chromatog.*, **23**, 245-252.
- Lee, A.L., Bartle, K.B., Lewis, A.C. (2001) A model of peak amplitude enhancement in orthogonal two-dimensional gas chromatography. *Anal. Chem.*, **73**, 1330-1335.
- Liu, Z., Phillips, J.B. (1991) Comprehensive two-dimensional gas chromatography using an on-column thermal modulator interface. *J. Chromatogr. Sci.*, **29**, 227-231.
- Marriott, P.J., Kinghorn, R.M. (1997) Longitudinally modulated cryogenic system. *Anal. Chem.*, **69**, 2582-2588.
- Mondello, L., Lewis, A., Bartle, K. (2002) *Multidimensional gas chromatography*, Ed. Wiley, London.
- Ong, R., Marriott, P. (2002) A review of basic concepts in comprehensive two-dimensional gas chromatography. *J. Chromatogr. Sci.*, **40**, 276-291.
- Phillips, J.B., Xu, J. (1995) Comprehensive multi-dimensional gas chromatography. *J. Chromatogr. A*, **703**, 327-334.
- Phillips, J.B., Gaines, R.B., Blomberg, J., van der Wielen, F.W.M., Dimandja, J.M., Green, V., Granger, J., Patterson, D., Racovalis, L., de Geus, H.J., de Boer, J., Haglund, P., Lipsky, J., Sinha, V., Ledford, E.B. (1999) A Robust Thermal Modulator for Comprehensive Two-Dimensional Gas Chromatography. *J. High Res. Chromatog.*, **22**, 3-10.
- Ruiz-Guerrero, R., Vendeuvre, C., Bertoncini, F., Thiébaud, D., Espinat, D. (2006) Comparison of two-dimensional gas chromatography coupled with sulfur- Chemiluminescence detector to standard Methods for Speciation of Sulfur-containing Compounds in Middel distillates. *J. Chromatogr. Sci.*, **44**, 566-574.
- Schoenmakers, P.J., Oomen, J.L.M.M., Blomberg, J., Genuit, W., van Velzen, G. (2000) *J. Chromatogr. A*, **892**, 29-46.
- Schomburg, G. (1995) Two-dimensional gas chromatography. principle, instrumentation, and methods. *J. Chromatogr. A*, **703**, 309-325.
- Vendeuvre, C., Bertoncini, F., Duval, L., Duplan, J.-L., Thiébaud D., Hennion M.-C. (2004) Comparison of conventional gas chromatography and comprehensive two-dimensional gas chromatography for the detailed analysis of petrochemical sample. *J. Chromatogr. A*, **1056**, 155-162.
- Vendeuvre, C., Ruiz-Guerrero, R., Bertoncini, F., Duval, L., Thiébaud, D., Hennion, M.C. (2005) Characterisation of middle-distillates by comprehensive two-dimensional gas chromatography (GC×GC): A powerful alternative for performing various standard analysis of middle-distillates. *J. Chromatogr. A*, **1086**, 21-28.
- Vendeuvre, C., Bertoncini, F., Espinat, D., Thiébaud, D., Hennion, M.C. (2005) Multidimensional gas chromatography for the detailed PIONA analysis of heavy naphtha: Hyphenation of an olefin trap to comprehensive two-dimensional gas chromatography. *J. Chromatogr. A*, **1090**, 116-125.
- Venkatramani, C.J., Xu, J., Phillips, J.B. (1996) Separation orthogonality in temperature-programmed comprehensive two-dimensional gas chromatography. *Anal. Chem.*, **68**, 1486-1492.

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