Comprehensive multi-dimensional chromatographic studies on the separation of saturated hydrocarbon ring structures in petrochemical samples

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Abstract

Characterization of complex petrochemical samples has been a classical subject of comprehensive two-dimensional (2D) gas chromatography (GC × GC). Macroscopic properties of these samples can be described accurately by separation of compounds in classes of identical molecular functionality. Ring structures in the carbon backbone of these compounds, which can be divided in saturated and unsaturated, are amongst the foremost functionalities affecting samples properties. Unfortunately, GC × GC tuned for separation of both saturated and unsaturated ring structures is likely to result in convoluted chromatograms when a distribution of both molecular properties is present in the sample. An independent liquid chromatographic (LC) separation preceding GC × GC could be used to resolve the mixture based on unsaturated rings, allowing saturated rings to be resolved separately in the GC × GC separation. This three-dimensional separation (abbreviated LC–GC × GC) was performed after rigorous evaluation of LC as part of a multidimensional separation using LC × GC. Group-type separation was achieved using this separation for components with either saturated or unsaturated rings. Results of this separation were used to compare information obtained by GC × GC with LC–GC × GC.
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1. Introduction

Characterizations of petrochemical streams are used to predict properties and/or behaviour in processes or during application. The amount of effort that has to be put into these characterizations depends on the desired level of information. Measurement of physical properties of the sample is one of the simplest forms of characterization. Indicative information on the aromaticity of a crude oil, for instance, can already be obtained from a single measurement of the density [1]. More information can be obtained by a separation based on the molecular properties of components in a sample. The hy-

drocarbons in a petrochemical sample can be separated into groups according to the number of aromatic rings using a standardized liquid chromatographic separation method [2], such as IP391. This characterization provides more information than the sole determination of density or total aromatic content, certainly when the quantitative nature of the results are considered.

With the advent of comprehensive two-dimensional (2D) gas chromatography (GC × GC) [3], even more information could be obtained compared to the above mentioned IP391 group type separation. Due to its two-dimensional nature, a hydrocarbon type separation can be obtained that also includes the volatility distribution within each class. An appropriate choice of the separation dimensions allows components of similar chemical structure to be readily grouped into bands, allowing rigorous group-type separations according to chemical class. Highly structured chromatograms of

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petrochemical samples are readily obtained using GC × GC based on separations along the distributions of volatility and polarity. The target groups of the saturated, mono-, di- and tri-aromatic species are separated by most commercially available medium-polar stationary phases applied in the second dimension, regardless of their type of interaction. Further classification within a group is difficult and only possible when specially tuned separation systems are used.

Only a few researchers have reported on the sub-classes of saturated cyclic hydrocarbons (naphthenics), despite their great importance from the petrochemical point of view. Selectivity between linear and cyclic alkanes has only been observed for phases that exhibit phenylic interactions. Application of these phases in GC × GC results in chromatograms that provide detailed group-type separation of both aromatics and naphthenics [4]. However, the gain in selectivity and resolution between linear alkanes and cyclic alkanes results in a loss of resolution between saturates and aromatics. In the chromatogram this becomes evident by overlap of some of the naphthenic and aromatic compounds. When classes overlap, structure is lost; if the classes remain separated, a structured separation pertains.

Overlapping classes and subsequent disordered chromatography prevent the efficient use of the unique selectivity of phenylic phases. Therefore, the separation system needs to be re-examined if ordered chromatograms are to be obtained. The requirements for a separation system capable of producing ordered chromatograms for specific samples have been fundamentally addressed by Giddings [5]. In this approach sample dimensionality is defined as the number of independent variables that must be specified to uniquely describe all components of the sample. Ordered chromatograms are considered the result of systematic and unambiguous elution of sample components according to these sample dimensions in multi-dimensional space. Unfortunately, the true dimensionality of complex samples, such as oil products, is very much larger than the number of separation dimensions that can possibly be employed. We achieve *apparent* structure by matching the *most-relevant* sample dimensions with a few separation mechanisms. Although GC × GC using a phenylic second-dimension phase succeeds in matching these sample dimensions, it fails to give the systematic distribution of aromatic and naphthenic classes. Phenylic phases display selectivity for both sample properties ("naphthenicity" and aromaticity), which results in a convoluted retention order that reflects neither property clearly. However, this convolution only results from insufficient resolution between saturates and aromatics. Within a class of compounds (e.g. saturates, aromatics) the dimensionality is lower than that of the entire sample. Therefore, the separation within a class may be ordered while that of the entire sample is not.

To regain a truly ordered separation according to three different sample dimensions, without the overlap of different cyclic species, a third dimension has to be added. The liquid chromatographic (LC) method used for group-type separa-

tion based on aromaticity is an attractive candidate for this dimension. In this separation, the sample dimensionality is effectively lowered by a group-type separation of the sample into compound classes with an equal number of aromatic rings. Systematic elution of naphthenic classes in subsequent GC × GC can then be achieved, allowing for ordered separation in a three-dimensional chromatogram. It is known that the selectivity of LC IP391 is based on interaction between the amino groups of the stationary phase and the aromatic π-electrons of specific analytes. However, no work has been published on the effect of saturated rings on the selectivity of this separation system. Because of this, the group-type separation of petrochemical samples containing both aromatic and naphthenic compounds is rigorously evaluated in this study. This will improve our understanding on how saturated rings affect LC elution.

This paper deals with the development of a comprehensive three-dimensional system, capable of separating cyclic hydrocarbon species in petrochemical samples that contain both aromatic and naphthenic compounds. At the same time, more-extensive knowledge is acquired on the retention mechanism of the IP391 NPLC method. Finally the feasibility of a three-dimensional separation system for the ordered separation of cyclic hydrocarbon group-types will be demonstrated. The discussion of this separation will include criteria whether (ordered) three-dimensional separations should be preferred over (less-ordered) two-dimensional separations.

2. Experimental

2.1. Samples, sampling and materials

A system calibration standard solution was prepared as prescribed in the IP391 method [2]. Cyclohexane (>99.9%), *o*-xylene (>99%), *n*-heptane (>98%) and 9-methylanthracene (>97%) were obtained from Merck. di-Benzothiophene (>99%) was obtained from Aldrich. The complex petrochemical sample used for all separations was diesel fuel, 5 μL of which was injected undiluted into the LC system. In some experiments, diesel with superadded trinaphthenes was used. Amounts of 3.50 mg perhydroanthracene and 4.60 mg perhydrophenanthrene, obtained from Shell's Westhollow Technology Center (Houston, TX, USA) were added to 485 mg diesel. The purity of both standards was determined to be >95% by GC–MS. Manual injection of 0.1 μL diesel with superadded trinaphthenes was used to obtain the GC × GC chromatogram of diesel.

Off-line coupling of the IP391 separation was performed by manual sampling of the effluent. Samples for subsequent analyses were collected after demounting the RI-detector to prevent extra-column band broadening. LC × GC sampling was performed at 0.2 Hz from $t = 2.60$ until $t = 11.27$, yielding 104 fractions overall. The backflush time (T_b) and resolution (R_s) were determined to be 12.67 and 7.72 min, respectively by separation of the system calibration standard. 1 μL of each

LC fraction was analyzed with 1D-GC. Because equal percentages of identically sampled fractions are transferred into the second dimension, this separation can be considered to yield a comprehensive chromatogram that is representative for the entire sample [6].

Group-type separation of diesel with superadded trinaphthenes was performed, resulting in collection of the saturates ($t = 2.75$–3.34), mono-aromatics ($t = 3.34$–4.48) and di-aromatics ($t = 4.48$–6.20). Separation of the system calibration standard resulted in $T_b = 7.55$ min and $R_s = 6.54$. Samples of the heart-cuts were injected using a CTC-PAL multipurpose sampler (CTC Analytics AG, Zwingen, Switzerland). One microliter was injected of the saturated class and 2 µL of the mono- and di-aromatic classes.

2.2. Instrumentation

For LC separations, a Shimadzu LC10-AD HPLC pump (Shimadzu Corporation, Kyoto, Japan) was used to deliver the mobile phase *n*-heptane (purity >98%, Merck Darmstadt, Germany) at a flow rate of 1 mL/min. A Shimadzu DGU-4A vacuum degasser was used to degas the solvent prior to use. A Shimadzu SIL-10A auto sampler was used to automatically inject volumes between 5 and 50 µL into a six-port valve equipped with a 50 µL sample loop. The LC column used was a 250 mm × 4.6 mm i.d. Phenomenex SphereClone, packed with 5 µm particles of amino-bonded silica (Phenomenex Inc., Torrance, CA, USA). It was kept at 40 °C in a Shimadzu CTO-10AC column oven. A Shimadzu SCL-10A system controller with option box was used for automation of the LC runs. RI-detection with a detector from Chrompack (Varian Chrompack International, Middelburg, The Netherlands) was used for the IP391 method; UV detection with a MicroUVIS 20 UV detector (Carlo Erba Instruments, Rodano (Milan), Italy) at 254 nm was used for determination of the band broadening effect of the RI-detector.

Gas chromatography for the LC × GC experiments was performed on a Mega 5300 series HRGC (Carlo Erba Instruments), equipped with an A200S auto sampler (Carlo Erba Instruments), Grob-type split-injector (300 °C) and a flame-ionization detector (350 °C). One microliter was injected in the hot split injector, using a split-flow of 20 mL/min. Helium was used as carrier gas at a constant inlet pressure of 125 kPa. GC analyses were performed on a 30 m × 0.10 mm i.d. DB-1 column with a film thickness of 0.1 µm (J&W Scientific Inc., Folsom, CA, USA). The temperature was programmed from 50 °C (5 min isothermal) to 325 °C at 10 °C/min.

The GC × GC system consisted of a 6890 series GC (Agilent Technologies, Avondale, PA, USA) configured with a CTC-PAL multi-purpose sampler (CTC Analytics AG, Zwingen, Switzerland), a Gerstel CIS-4 PTV injector (Gerstel GmbH & Co.KG, Mülheim an der Ruhr, Germany) and a flame-ionization detector. Split injection was performed using an inlet pressure of 250 kPa and total flow of 117 mL/min. After injection, the PTV liner was heated to 250 °C at 12 °C/s. Ten minutes after injection, the PTV

is cooled back to its standby temperature of 40 °C. A loop-type cryogenic modulator (ZOEX Corp., Lincoln, NE, USA), set to a modulation time of 7.5 s, and a second dimension column oven (ZOEX) were installed to enable flexible GC × GC. The column-set used consisted of 10 m × 0.25 mm i.d. DB-1, a dimethylpolysiloxane column with a film thickness of 0.25 µm (J&W Scientific Inc., Folsom, CA, USA) used as first dimension, a 2 m × 0.1 mm i.d. DPT-MDS deactivated fused-silica modulation capillary (BGB Analytik AG, Adliswil, Switzerland) and a 2 m × 0.10 mm i.d. BPX-50, a 50% (eq.) polysilphenylene-siloxane column with a film thickness of 0.10 µm (SGE, Ringwood, Australia) as second dimension. Columns were coupled with press-fits (Techrom, Purmerend, The Netherlands). The GC oven was programmed from 40 °C (5 min isothermal) to 300 °C (10 min isothermal) at 5 °C/min. The second-dimension column temperature was maintained 50 °C above that of the first-dimension column during the entire experiment.

2.3. Data processing

The detector signals of all chromatographic methods were recorded with EZChrom Elite software, Version 2.61, SP1 (Scientific Software Europe, Willemstad, The Netherlands). The acquisition rate for the RI, UVIS and 1D-GC was set to 5 Hz, GC × GC data was collected at 100 Hz to obtain a sufficient number of data points across a peak. The LC and 1D-GC chromatograms were processed in EZChrom Elite. MatLab Version 6.5 (The MathWorks, Natick, MA, USA) was used for conversion of the linear signal into two-dimensional data matrices. GC × GC data was processed and visualized with in-house developed software [7]. LC × GC data was visualized using Noesys Transform v. 3.0 (Research Systems Inc., Boulder, CO, USA).

3. Results and discussion

As outlined in the introduction section, the main goal of the current paper is to obtain three-dimensional information on complex petrochemical samples in order to resolve cyclic alkanes from linear alkanes and from aromatic compounds. GC × GC using a phenylic phase in the second separation dimension was found inadequate for this purpose, because of the selectivity for both aromatic and naphthenic ring structures that prevents separation of the desired classes. Ordered chromatograms of these samples require independent separation based on volatility, the number of aromatic rings and the number of naphthenic rings. Therefore, LC group-type separation based solely on aromatic ring structures was suggested as an independent separation dimension preceding GC × GC. Successful application in a multi-dimensional system requires totally resolved target groups, which can be can be collected separately. NPLC according to the IP391 protocol, modified for subsequent GC analysis, was studied in

respect of these requirements. Separation of a diesel fuel by comprehensive LC × GC separation will be demonstrated.

3.1. Evaluation of NPLC as a dimension in a three-dimensional separation system

The sample used for examination of the IP391 separation was a diesel fuel. Its significant amount of aromatic and naphthenic compounds was required to demonstrate the separation of both classes. According to the IP391 method, the column was back-flushed after elution of the di-aromatics. The only deviation from the published method was the undiluted injection of the sample, to ensure that concentrations in the effluent were suitable for split injection in subsequent GC separations. The injection volume used was close to the maximum loadability of the analytical column. Experimental parameters for the LC and the comprehensive LC × GC separations were kept identical to allow comparison, except for removing the refractive index detector in the LC × GC experiment.

A reasonable separation between the saturates, mono- and di-aromatics in the sample is evident from the LC chromatogram in Fig. 1. The narrow elution profile of the saturated compounds suggests unretained elution of this class, while the mono- and di-aromatic classes may be broadened by secondary retention mechanisms. Lack of chromatographic resolution gives rise to incomplete separation between the saturated and mono-aromatic compounds. The poor chromatography evident from Fig. 1, however, is most likely exaggerated by extra-column band broadening resulting from the large amount of injected sample and the large cell volume of the refractive-index detector. Though, overloaded chromatography cannot be excluded judging from this figure. The separation between mono- and di-aromatics is almost complete.

Comprehensive coupling of LC to GC is a rigorous way to gain insight into the parameters affecting LC retention. Using LC × GC, we can discriminate between chromatographic overloading and band broadening in the LC dimension as a result of secondary interactions. The LC effluent was collected until the back-flush point. No poly-aromatic fractions were analyzed, since the back-flushed effluent does not contain information regarding the LC separation. The GC data obtained on the individual LC fractions were combined into a 2D contour plot, similar to those commonly constructed for GC × GC. The analogy between LC × GC and GC × GC is further emphasized by plotting the LC dimension along the *y*-axis and the GC dimension along the x-axis. This results in chromatograms with similar separation mechanisms (volatility versus polarity) along each axis (Fig. 2). Since the main interest in a comparison focuses on the separation mechanisms, this representation proved to be more convenient than the standard representation. LC × GC and GC × GC chromatograms of the diesel sample are presented in Figs. 3 and 4.

The elution of aromatic classes as observed in Fig. 1 is reflected by the three separate bands in the LC × GC chromatogram. The aromatic classes appear to be well separated using LC × GC, in contrast to the incompletely resolved groups in LC. Lack of chromatographic resolution in Fig. 1, resulting in the incomplete separation of aromatic classes, can thus largely be attributed to extra-column broadening in the backflush valves or refractive-index detector. Only minimal tailing due to overloading is observed in the LC dimension. The tailing peaks from some of the saturated compounds in the LC dimension are those of the linear alkanes, which are the most abundant compounds in the sample. This effect, however, is not a major obstacle for use of LC in the first dimension. Any carry-over into the class of mono-aromatics is unlikely to result in co-elution in GC × GC.

A most important prerequisite for application of the IP 391 LC method in a three-dimensional separation system is the unambiguous elution of classes according to the number of aromatic ring structures. Other functional groups, especially naphthenics, should not induce carry-over between different aromatic target-groups. Selectivity for naphthenics in GC × GC using phenylic phases in the second dimension was shown to result in less ordered separations (Fig. 4). To assure the indiscriminate elution of naphthenics from the LC dimen-
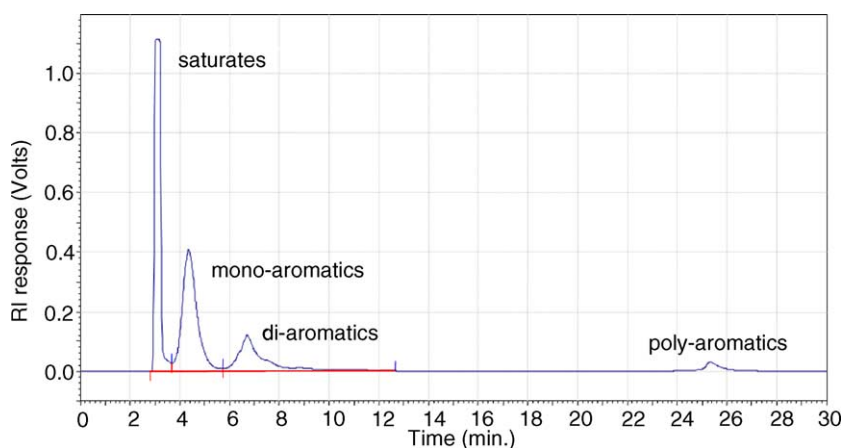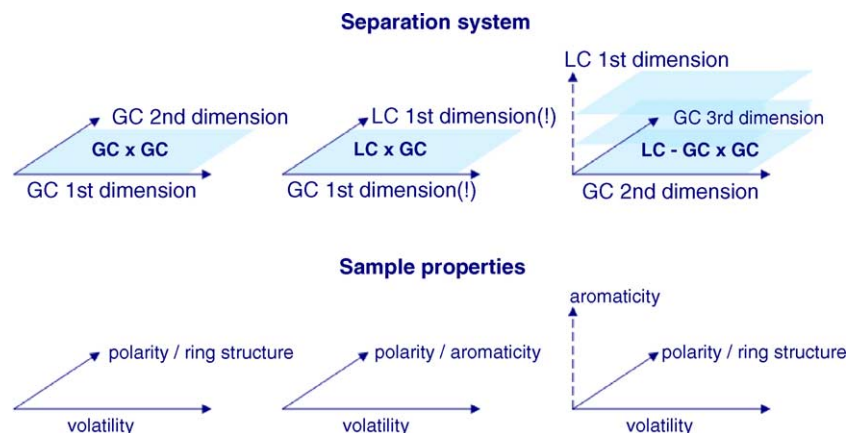

Fig. 1. Preparative separation of 5 μL diesel by IP391.

Fig. 2. Separation dimensions in GC × GC, LC × GC and LC–GC × GC as displayed in this paper.

sion, a diesel sample with two superadded trinaphthenic compounds was analysed with LC × GC. A comparison of the chromatograms with and without superadded trinaphthenic compounds confirmed that no selectivity for this class was exerted.

From Fig. 3, which zooms in to the parts of the LC × GC chromatograms where the tri-naphthenic compounds elute, it is evident that these compounds elute together with the other saturated compounds. Different LC peak widths in the figures are the result of in phase/out phase sampling over the LC elution profile. This effect is not relevant for the actual separation and can thus be ignored. All six structural isomers (resulting from cis/trans isomerism) of perhydrophenantrene and perhydroanthracene elute with the saturates. Some of them are well visible, while others co-elute with (generally higher concentrated) saturated-compounds. We conclude from these results

that no selectivity for cyclic alkanes is exerted in a separation according to the IP391 method.

3.2. Group-type collection of diesel components based on aromaticity

We have demonstrated that LC according to the IP391 method meets the requirements for application in a multi-dimensional separation system. Individual aromatic classes can be collected up to the di-aromatic class by operation of this method is a heart-cut mode. In this form, LC will be employed in a three-dimensional separation, in which components are resolved according to their aromatic class prior to analysis by GC × GC. Due to the heart-cutting nature in which the first dimension is operated, this separation is abbreviated as LC–GC × GC [6]. The separation is demonstrated
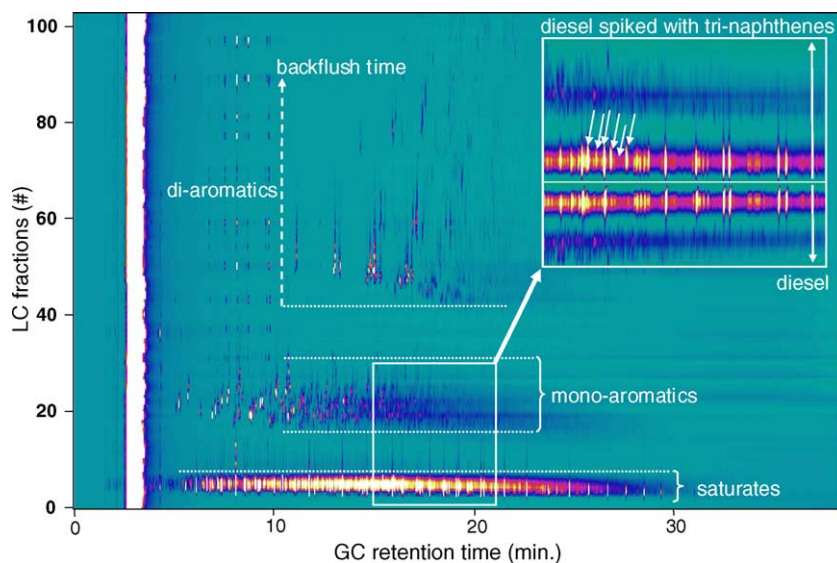

Fig. 3. LC × GC of diesel fuel. Clear separation between aromatic group types in LC × GC. The magnified part of the chromatogram presents the elution of tri-naphthenics.
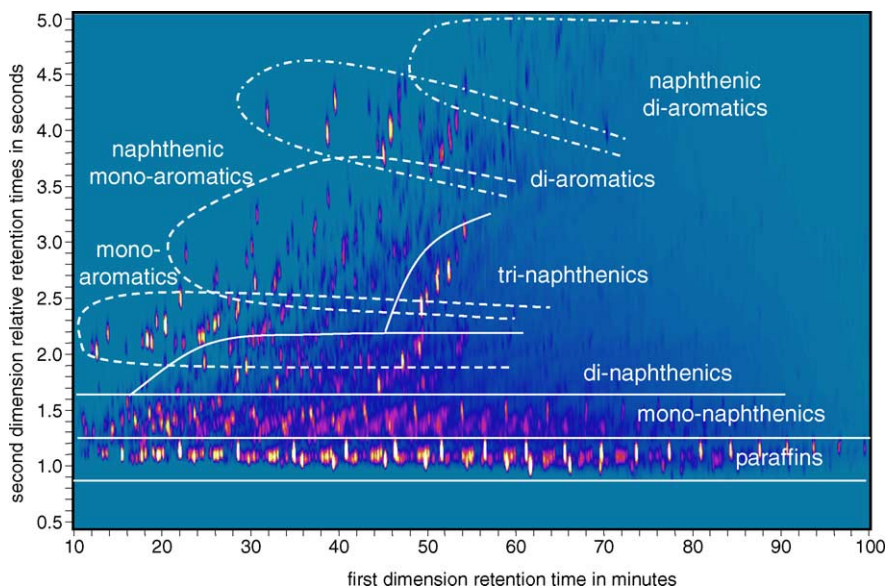
Fig. 4. GC × GC chromatogram diesel, identification tentative.

using the same diesel sample with superadded tri-cyclic alkanes, which was also separated by LC × GC and GC × GC. Experimental parameters for the LC separation remained unchanged, except for the effluent sampling.

In order to obtain the saturated, mono- and di-aromatic classes from the LC separation, the effluent was collected continuously from the moment of first elution until most of the di-aromatic compounds had eluted. Cut-times for the effluent collection were determined prior to fractionation using refractive index detection. The valleys between different classes in the detector signal marked the time for switching their collection. An issue regarding the LC group-type separation was the dilution due to selectivity within aromatic classes. Selectivity within the di-aromatics resulted in nearly a five-fold increase of its elution volume compared to the saturates. This dilution increases the concentration difference between aromatic classes even more since in diesel fuel components generally become less abundant with increasing aromaticity. Analysis of excessively diluted mono- and di-aromatic classes would require the optimization of a large-volume technique for GC × GC, making the separation overly complex for its purpose. Use of preparative LC equipment could have solved concentration related issues, but was also considered as being beyond the scope of this exploratory research. Therefore, collection of the di-aromatics was cut off about halfway the elution domain specified by the IP391 method. The concentration within this class could thus be increased by a factor of two at the cost of losing a negligible amount of di-aromatic compounds. GC × GC analysis of di-aromatic heart-cuts collected according to IP391 and the modified sampling method confirmed that the modified sampling did not affect conclusions about the performance of the IP391 as part of a three-dimensional separation, as the modifications only affected the concentration of some di-aromatic

compounds eluting after 4.5 s relative second dimension retention time (Fig. 7).

3.3. Three-dimensional separation performance

GC × GC chromatograms of aromatic classes could be obtained with satisfactory signal-to-noise ratios thanks to modifications to the LC group-type sampling and increased injection volumes for mono- and di-aromatic compounds for GC × GC analysis (Figs. 5 through 7). The color scale of these contour plots has been optimized for maximal contrast in each chromatogram separately, thus does not represent any quantitative relation between these chromatograms. Separation of aromatics classes is observed to be almost complete, only some linear alkanes are present in the mono-aromatic fraction. This phenomenon has already been elucidated in the discussion of the LC × GC results, where extra-column band broadening was observed to result in carry-over of these compounds into the mono-aromatic elution domain. Because the linear alkanes are fully resolved from the mono-aromatics, their presence is irrelevant for conclusions to be drawn about separation within this class. Information that can only be obtained with LC–GC × GC has been indicated with the line in Fig. 5, which marks the lower second-dimension retention of the mono-aromatic class. Compounds eluting above this line cannot be resolved from mono-aromatics using GC × GC. Mono-aromatic compounds that were separated from di-aromatic compounds are presented in a similar way in Fig. 6.

Elution-patterns that could not be observed in a GC × GC separation are revealed in the chromatograms of individual aromatic classes. In Fig. 5 the separation of naphthenic classes is demonstrated to extend beyond the linear and mono-naphthenic alkanes. di-Naphthenic and even tri-naphthenic alkanes, which would have overlapped with
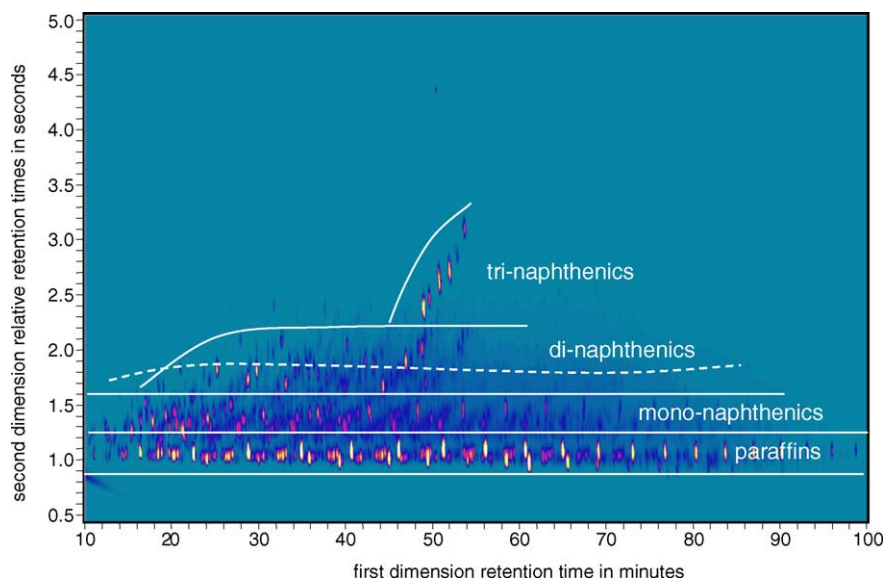
Fig. 5. LC–GC × GC chromatogram of the saturated compounds from diesel.

mono-aromatic compounds in a GC × GC separation, are re-solved from each other and can be separated according to the number of naphthenic rings. Another interesting obser-vation from Fig. 5 relates to the structured elution within naphthenic classes. Linear and mono-naphthenic saturates elute in an ordered fashion, but this order appears to have degraded for the di-naphthenic saturates. Structured elution in so-called roof tiles, as observed for linear and mono-naphthenic alkanes, distinguishes components in sub-classes based on their functional groups and the number of car-bon atoms. Components eluting in the same roof-tile are structural isomers, their position in the roof tile depends on the branching or shape of the molecule [4]. Roof-tiled elu-tion is also apparent for the di-naphthenics, but the com-

ponents are not sufficiently separated to obtain the same information compared to linear and mono-naphthenic satu-rates. Disordered separation, for example as observed for the C_{12} and C_{13} di-naphthenics eluting between 32 and 44 min, prevents the components to be assigned to either sub-class. The increased chromatographic disorder presumably finds its origin in the presence of five and six membered naph-thenic rings and cis/trans isomerism of these ring structures. These sample dimensions are not unlikely to result in the de-graded order of this class, considering the shape selectivity of the separation. Even though the local disorder observed for di-naphthenic compounds, separation between naphthenic classes is preserved. Judging from the observed selectivity between naphthenic classes higher classes of naphthenics
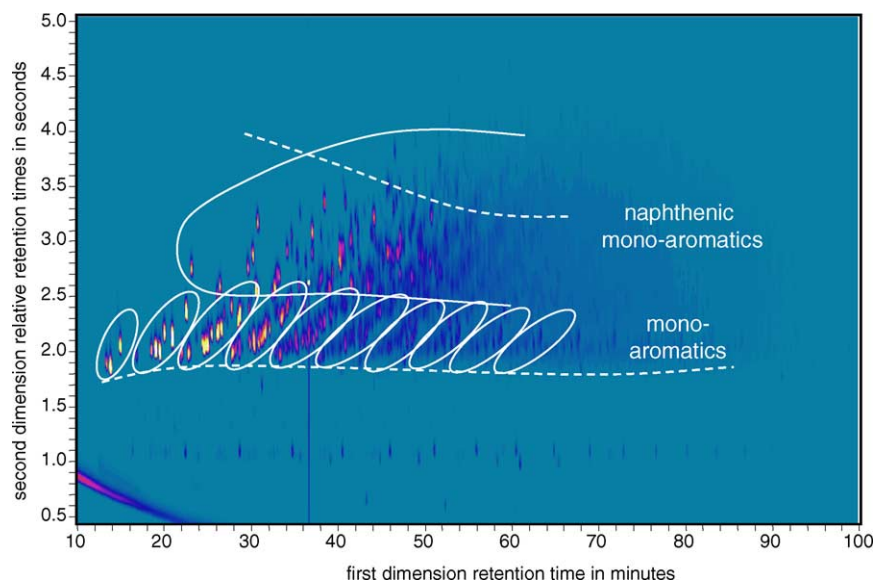

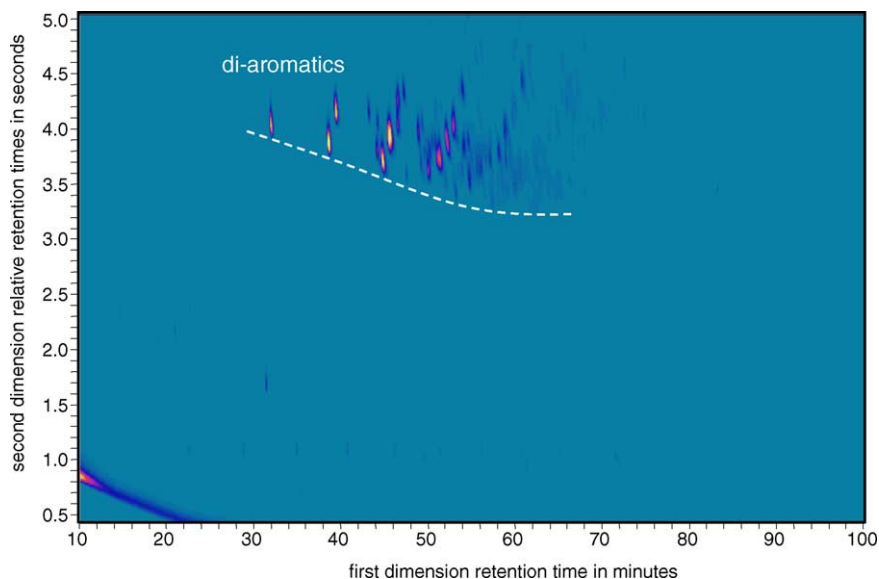Fig. 6. LC–GC × GC chromatogram of the mono-aromatic compounds from diesel.

Fig. 7. LC–GC × GC chromatogram of the di-aromatic compounds from diesel.

could also be resolved using this set-up. Separation of a sample with enough isomers of these classes is required to prove this.

The chromatogram of the mono-aromatics (Fig. 6) as a whole appears less ordered compared to that of the saturates. Structured elution is only observed for the linearly substituted aromatic compounds, which appear as the roof-tiles between 2.0 and 2.5 s second-dimension retention time. Above these compounds, mono-aromatics elute that also contain naphthenic rings in the carbon backbone. These bi-functional compounds cannot be resolved from the class of linearly substituted mono-aromatics and no systematic elution pattern is observed for this class. Linearly substituted mono-aromatics can only be recognized, because of the ordered elution within this class. Obviously, the retention characteristics are affected beyond the selectivity of this separation system by substitutions of the functional groups. Another argument for the lack of structure for naphthenic aromatics is that not enough isomers within each group of compounds are available for structured elution to be apparent. The vague roof tiles observed for naphthenic mono-aromatics with higher carbon numbers are far from ordered sufficiently for any sub-class to be resolved.

The structure within the di-aromatics did not come unexpected since it was already observed in the Fig. 4. This is, of course, implied by the composition of the sample, which obviously does not contain much naphthenic di-aromatics. Because of the simple, non-cyclic substitutions for most of the di-aromatics observed here (Fig. 7), resolution between the components as well as the groups is excellent. A third separation-dimension does not add information by separating any of the observed di-aromatic compounds, but contributes to the separation result by removing the overlapping mono-aromatics.

4. Conclusions

The LC method that was identified for group-type separation of complex hydrocarbon mixtures based on aromaticity was found suitable for this application. Information obtained by LC × GC was used for obtaining extensive information about this LC method. Besides demonstration of aromatic group-type separation, LC × GC results were used to obtain critical information on separation of naphthenic compounds and to explain chromatographic band-broadening of saturated compounds. Naphthenic compounds were found to have no interaction with the stationary phase of the LC separation, thus allowing this separation to be used in an LC–GC × GC set-up where these compounds are resolved from aromatics in an independent separation.

LC–GC × GC separation was demonstrated successfully in providing information on the elution order of naphthenic and aromatic compounds, which remain partially convoluted in a GC × GC separation. Group-type separation of naphthenic alkanes was obtained for all naphtenic alkanes available in diesel. The selectivity observed for these classes suggests that separation of tri-naphthenics or even higher naphthenics with the current system is plausible. However, removal of the mixed dependency between naphthenic and aromatic classes reveals new dependencies or sample dimensions, which influence systematic elution of the separation and the order observed in resulting chromatograms. Elution of di-naphthenic compounds was found to be less ordered compared to linear and mono-naphthenic alkanes, presumably because of the increasing number isomers resulting from C_5/C_6 naphthenic rings and cis/trans isomerism.

Although ordered elution of linearly substituted mono-aromatics is apparent, which reveals their identity in this partially convoluted separation, no indisputable separation

is achieved between these compounds and naphthenic mono-aromatics. Insufficient selectivity of the phenylic stationary phase in GC × GC between linearly and naphthenic substituted mono-aromatics resulted in overlap of both classes of compounds. Separation of di-aromatic compounds experienced no significant improvement of the three-dimensional separation due to lack of overlap with naphthenic aromatics.

The value of IP391 LC as an extra separation dimension for complex (petrochemical) samples other than diesel depends on whether naphthenic and aromatic target-groups can be separated. LC–GC × GC can provide structured chromatograms for naphthenic classes where GC × GC can not. GC × GC separation requires less time and equipment, while providing a quantitative overview of the entire sample.

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